ALLEN'S
COMMERCIAL ORGANIC ANALYSIS

FOURTH EDITION REWRITTEN AND REVISED

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THE AMERICAN ELECTRO-CHEMICAL SOCIETY; MEMBER AMERICAN
INSTITUTE OF CHEMICAL ENGINEERS.

IN many respects this edition of Allen is a new work. The field of Commercial
Organic Analysis has been so enlarged and specialised during the last few years
that it has been found necessary to rewrite many parts and add much new matter.
Obsolete methods are omitted; what little of the old text remains has been care-
fully revised and many new illustrations added.

To accomplish the object in view, namely, the furnishing of a modern work
of the greatest practical value to the analyst, it was deemed advisable to secure
the services of an English and an American editor and to organise a corps of
writers particularly versed in the subjects discussed.

The general arrangement of the volumes remains as before, only such changes
have been made as will bring the text into line with the latest scientific classi-
fication. Great care has been exercised by the editors and contributors in the
choice of methods and only those of the highest degree of accuracy and rapidity
selected. Effort has been made to secure uniformity in weights and measures,
nomenclature and abbreviations. References are to original sources, not to
translations or abstracts.

The work is issued in nine volumes, numbered consecutively, as follows:

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ALLEN'S

COMMERCIAL ORGANIC ANALYSIS

VOLUME IV

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ALLEN'S COMMERCIAL

ORGANIC ANALYSIS

A TREATISE ON

THE PROPERTIES, MODES OF ASSAYING, 'AND PROXIMATE
ANALYTICAL EXAMINATION OF THE VARIOUS
ORGANIC CHEMICALS AND PRODUCTS
EMPLOYED IN THE ARTS, MANU-
FACTURES, MEDICINE, Etc.

'WITH CONCISE METHODS FOR

THE DETECTION AND ESTIMATION OF THEIR IMPURITIES,
ADULTERATIONS, AND PRODUCTS OF DECOMPOSITION

VOLUME IV

Resins, India-Rubber, Rubber Substitutes and Gutta-Percha, Hydrocarbons
of Essential Oils, Ketones of Essential Oils, Volatile or Essential Oils,
Special Characters of Essential Oils, Tables of Essential Oils

BY THE EDITORS AND THE FOLLOWING CONTRIBUTORS

M. BENNETT BLACKLER   E. W. LEWIS   T. MARTIN LOWRY
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P. BLAKISTON'S SON & CO.

1012 WALNUT STREET

PREFACE.

By dividing the section of Essential Oils so as to have the several portions written by those who are authorities on the subject it has been possible to arrange the text so that the users of the book will find it more satisfactory for reference.

As far as practicable the general methods of analysis applicable to groups of compounds such as the resins or the essential oils, having the same general constituents, are treated in the general discussion, while individual peculiarities are treated in the detailed discussion.

This volume has been carefully rewritten and contains much new matter. This is particularly true of the sections treating upon general methods of analysis and investigation of Resins, India-rubber and of the important constituents of Essential Oils. Special acknowledgment should be made here for the work done on the previous edition of this volume by Mr. A. R. Tankard, who devoted much time and care to its preparation. This was some of the most recent work done on Allen prior to this edition.

The editors wish to take this opportunity of thanking the contributors to this volume for their very thorough work of revision.

All temperatures quoted are *Centigrade* unless otherwise specified.

The term "optical rotation" in this volume represents the observed angular rotation at 15° C. for 100 millimetres of the liquid, the sign $[a]_D$ denoting the specific rotation of the substance for sodium light (D-ray).

As in previous volumes in the absence of any statement to the contrary all specific gravities refer to a temperature of 15.5° C. compared with water as unity at the same temperature.

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ERNEST J. PARRY.

SPECIAL CHARACTERS OF ESSENTIAL OILS.

HENRY LEFFMANN AND CHARLES H. LAWALL.

RESINS.

By M. BENNETT BLACKLER, Ph. D.

The *resins* form a group of substances of very complex and variable chemical composition, but having somewhat similar physical characters.

Various substances or mixtures having the general physical characters of resins are obtainable artificially, but all the more important members of the class are natural products.

The natural resins occur, as a rule, in exudations from plants, which exudations are sometimes normal and natural, and in other cases the result of diseased conditions. The exudation of these resinous products may often be induced artificially.

The resins sometimes occur naturally in admixture with gummy matter, essential oils, etc. Resinous products which contain much gum or allied substances—as is the case with asafœtida, galbanum, and ammoniacum—are called *gum-resins*. Similarly, such natural products as consist of solutions or emulsions of resins in essential oils are called *oleo-resins*, or sometimes *balsams* or *turpentines* (page 74).

CHEMICAL COMPOSITION OF RESINS.

Even when separated from the gums, oils, and other substances with which they frequently co-occur in nature, the resins are rarely, if ever, pure chemical compounds. They consist of a mixture of several bodies, the chemistry of which until recently was very obscure.

The resins were formerly regarded as oxidation-products of terpenes, but while this is true of some of them, it is by no means a general rule. According to the researches of Doebner, certain resins are chiefly composed of condensation-products of aromatic aldehydes and phenols; but an accurate knowledge of the chemistry of resins is chiefly due to the recent researches of A. Tschirch, who points out that the proximate constituents of resins, so far as they are known, may be classified under the following three heads: *Resin-esters* and their decomposition-products; *Resinolic* or *Resin Acids;* and *Resenes;* the last being

substances of indifferent or unknown constitution. **In many of the**
resins one or other of these classes preponderates, and the product
consequently falls into the group of *ester-resins, acid-resins,* or *resene-
resins.* Representatives of all three classes are rarely present in the
same product.

For the proximate analysis of resinous substances, Tschirch dissolves
the sample in ether and agitates the solution successively with 1. A 1%
solution of ammonium carbonate; 2. A 1% solution of sodium carbon-
ate; and 3. Solutions of potassium hydroxide of 0.1 and 1.0%. These
reagents dissolve the resin-acids, which can be precipitated from the
alkaline liquids by a dilute mineral acid. On subjecting the ethereal
solution to steam-distillation, any essential oil will volatilise, together
with the ether. The residue may contain resin-esters and resenes,
which can be separated by saponification with alcoholic potassium
hydroxide, when the acid-radicals of the esters will form soluble
potassium salts, and the resenes and resin-alcohols can be extracted by
agitation with ether. The resin-alcohols can be acetylated or ben-
zoylated, whereas the resenes resist such treatment.

Among the resins in which resin-esters predominate, Tschirch
includes 1. The *benzo-resins,* gum-benzoin, Peru and Tolu balsams,
storax, acaroid-resins, aloes resin, and dragon's blood; and 2. The
umbelliferous gum-resins, ammoniacum, galbanum, sagapenum, asafœ-
tida, and umbelliferous opopanax.

The *terpeno-resin,* consisting chiefly of resin-acids, include the vari-
ous coniferous resins, copaiba balsam, and the resin of Zanzibar copal.

The resinous materials in which *resenes* predominate include 1. The
burseraceous oleo-resins, myrrh, olibanum, bdellium, burseraceous
opopanax, Mecca balsam, various elemis, tacamahaca, and mastic;
and 2. The dipterocarpus products, Doona resin, dammar, and Manila
copal.

Resin Esters.

As a rule, the esters of the resins yield on saponification aromatic
acids, such as benzoic and cinnamic acids. These resins consequently
come under the denomination of *aromatic balsams,* and as such have
already been described. Amber, however, contains succinic acid,
which is a compound of the aliphatic series.

Benzoic acid, $C_6H_5.COOH$, occurs in Peru and Tolu balsams,
Siam benzoin, and (together with benzoyl-acetic and probably phenyl-
hydracrylic acid) in dragon's blood.

Cinnamic acid, $C_6H_5.CH:CH.COOH$, is present in Peru and Tolu balsams, storax, yellow acaroid resin, and Sumatra benzoin.

Salicylic acid, $C_6H_3(OH).COOH$, has been found in gum ammoniacum.

p-Coumaric acid, $C_6H_4(OH)^{(1)}.CH:CH.COOH^{(1)}$, is present in yellow and red acaroid resins.

Ferulic ▪ acid, $C_6H_3(OH)^{(1)}.(OCH_3)^{(2)}.CH.COOH$, occurs in asafœtida.

Umbellic acid, $C_6H_3(OH)^{(2)}(OH)^{(3)}.CH:CH.COOH_3$, occurs together with its anhydride *umbelliferone*, in sagapenum, galbanum, and asafœtida.

Resin Alcohols.

The alkyl-radicals of the resin-esters were practically unknown until recently, but the researches of A. Tschirch and his collaborators have resulted in the isolation of the following resin-alcohols. Tschirch distinguishes two kinds of these—*resinols* and *resinotannols*. The members of the former group are colourless and give no tannin-reaction with iron salts, while the latter are coloured and give a tannin-reaction.

Resinols	Occurrence	Formula	M. p.	Observers.
a- and β-amyrin	Elemi	$C_{30}H_{49}(OH)$		Vesterberg.
Benzoresinol	Benzoin	$C_{16}H_{26}(OH)O$	$274°$	Tschirch and Ludy.
Chironol	Burseraceous opopanax.	$C_{28}H_{47}(OH)$	$173°$ to $176°$	Tschirch and Baur.
Pinoresinol	Pine resin	$C_{18}H_{18}O_6$	$80°$ to $90°$	Bamberger.
Storesinol	Storax	$C_{12}H_{20}O$ or $C_{36}H_{58}O_3$		von Miller.
Succinoresinol	Amber	$C_{12}H_{20}O$	$275°$	Tschirch and Aweng.

The table of *resinotannols* is given on page 4.

In cases where such substances have been obtained, the products of acetylation and benzoylation of the resinotannols all contain one acetyl- or one benzoyl-group, with the exception of the product of benzoylation of aloresinotannol, which contains 2 benzoyl-groups in the molecule.

Resinolic Acids.

These compounds are the characteristic free acids of resins, and are, in general, substances of complex constitution and high molecular weight. They usually contain one or more hydroxyl-groups as well as carboxyl-residues. Besides the many acids stated by Tschirch to exist in coniferous oleo-resins (page 79), the resin-acids tabulated on page 5 have been described.

TABLE OF RESINOTANNOLS.

Resinotannols	Occurrence	Formula	Acid product of treatment with nitric acid	Product of fusion with potassium hydroxide	Observers
Aloresinotannol	Cape aloes[1]	$C_{22}H_{26}O_6$.	Styphnic acid	Resorcinol	Tschirch and Pedersen.
Ammoresinotannol	Ammoniacum	$C_{16}H_{22}O_2(OH)$.	Picric acid		Tschirch and Luz.
Asaresinotannol	Asafœtida	$C_{24}H_{34}O_5$.			Tschirch and Polasek.
Dracoresinotannol	Palm dragon's blood	$C_8H_9O(OH)$; or $C_{24}H_{30}O_4$.			Tschirch and K. Dieterich.
Erythroresinotannol	Red acaroid	$C_{40}H_{40}O_{10}$.	Picric acid		Tschirch and Hildebrand.
Galbanoresinotannol	Galbanum	$C_{18}H_{29}O_2(OH)$.	Camphoric and camphoronic acids.		Tschirch and Conrady.
Oporesinotannol	Umbelliferous opopanax.	$C_{12}H_{13}O_2(OH)$.	Oxalic and picric acids.		Tschirch and Knitl.
Panaxresinotannol	Burseraceous opopanax.	$C_{34}H_{40}O_7(OH)$.			Tschirch and Baur.
Peruresinotannol	Peruvian balsam	$C_{18}H_{19}O_4(OH)$.	Oxalic and picric acids.		Tschirch and Trog.
Sagaresinotannol	Sagapenum	$C_{24}H_{27}O_4(OH)$.	Styphnic acid		Tschirch and Hohenadel.
Siaresinotannol	Siam benzoin	$C_{12}H_{13}O_2(OH)$.	Picric acid		Tschirch and Lüdy.
Sumaresinotannol	Sumatra benzoin	$C_{45}H_{19}O_3(OH)$.	Picric acid	Protocatechuic acid.	Tschirch and Lüdy.
Toluresinotannol	Tolu balsam	$C_{17}H_{17}O_4(OH)$.	Oxalic and picric acids.	Protocatechuic acid.	Tschirch and Obervander.
Xanthoresinotannol	Yellow acaroid	$C_{43}H_{46}O_{10}$.	Picric acid		Tschirch and Hildebrand.

[1] Tschirch and Klaveness (*Arch. Pharm.*, 239, p. 241) have recently examined the resinotannol of Uganda aloes, the resin of which is a compound of p-coumaric acid with Uganda-resinotannol, $C_{21}H_{22}O_3$. This resinotannol is identical with that of Natal aloes.

TABLE OF RESINOLIC ACIDS.

Resin acids	Occurrence	Formula	M. p. °	Observers
Agaric		$C_{16}H_{30}O_5 + H_2O$	138 to 139	Jahns.
Aleuritic	Shellac	$(C_{13}H_{26}O)n$	101.5	Tschirch and Farner.
Callitrolic		$C_{64}H_{82}O_5(OH)(COOH)$	248	Tschirch and Balzer.
		$C_{30}H_{48}O_5$		T. A. Henry.
Copaivic[1]	Copaiba balsam	$C_{20}H_{30}O_2$		Schweitzer.
Dammarolic	Dammar	$C_{54}H_{77}O_3(OH)(COOH)_2$		Tschirch and Glimmann.
Guaiacic	Guaiacum	$C_{20}H_{24}O_4$	75 to 80	Döbner and Lücker.
Guaiaconic	Guaiacum	$C_{20}H_{24}O_5$	95 to 100	Döbner and Lücker.
Illuric	African copaiba	$C_{20}H_{28}O_3$	1?8	Tschirch.
Pimaric (inactive)	Sandarac	$C_{20}H_{30}O_2$	171	T. A. Henry.
Podocarpic	Podocarpin resin	$C_{17}H_{22}O_3$	187 to 188	Oudemans.
Sandaracolic	Sandarac	$C_{43}H_{61}O_3(OCH_3)(OH)(COOH)$	140 (152)	Tschirch and Balzer.
Succinoabietic	Amber	$C_{80}H_{120}O_5$	148	Tschirch and Aweng.
Trachylolic	Zanzibar copal	$C_{56}H_{88}O_8$	165	Tschirch and Stephan.
Iso-trachylolic	Zanzibar copal	$C_{56}H_{88}O_8$	105 to 107	Tschirch and Stephan.
Elemic	Elemi	$C_{35}H_{46}O_4$		Flückiger.
Boswellic	Olibanum	$C_{32}H_{52}O_4$	142 to 150	Tschirch and Halbey.
Chronolic	Burseraceous opopanax	$C_{28}H_{48}O_4$	100 to 108	Tschirch and Baur.
α-Masticic	Mastic	$C_{23}H_{36}O_4$	90 to 91	
β-Masticic	Mastic	$C_{23}H_{36}O_4$	89.5 to 90.5	Tschirch
Masticolic	Mastic	$C_{23}H_{36}O_4$	201	and
α-Masticonic	Mastic	$C_{32}H_{48}O_4$	96 to 96.5	Reuter.
β-Masticonic	Mastic	$C_{32}H_{48}O_4$	91 to 92	

[1] Meta- and oxy-copaivic acids, and probably also several isomeric copaivic acids, are said to occur in the different varieties of copaiba.

Certain relations, more or less fanciful, can be traced between some of the resin-acids, by consideration of their reputed formulæ, which, however, must not, in most cases, be regarded as very positively ascertained.

None of the resin-acids appear to contain more than one hydroxyl-group; but while sandaracolic and podocarpic acids contain only one carboxyl-group, two such groups appear to exist in the molecules of abietic, succino-abietic, trachylolic, and dammarolic acids.

Resenes.

These substances are practically unclassifiable. They are oxygenated compounds, but are not acted on by alkalies and possess no characteristic chemical properties. They do not appear to be alcohols, esters, acids, ketones, or aldehydes. They are insoluble in and unacted on by alkali hydroxides, a fact which gives the resins containing them one of their chief values for the manufacture of varnishes. The following are among the resenes which have been described by Tschirch and his co-workers:

Resene.	Occurrence.	Formula.	M. p. °	Observers.
Alban..............	Gutta-percha ...	(?) $C_{40}H_{64}O_3$.	195	Tschirch and Oesterle.
α-Copalresene........	Copal..........	(?) $C_{25}H_{38}O_4$.	75 to 77	Tschirch and Stephan.
β-Copalresene........	Copal..........	$C_{25}H_{38}O_4$.	....	Tschirch and Stephan.
α-Dammarresene ...	Dammar........	(?) $C_{33}H_{52}O_3$.	65	Tschirch and Glimmann.
β-Dammarresene....	Dammar........	$C_{31}H_{52}O$.	206	Tschirch and Glimmann.
Dracoalban.........	Palm Dragon's blood.	$C_{20}H_{40}O_4$.	....	Tschirch and K. Dieterich.
Dracoresene........	Palm Dragon's blood.	(?) $C_{26}H_{44}O_2$.	74	Tschirch and K. Dieterich.
Fluavil.............	Gutta-percha ..	(?) $C_{40}H_{64}O_4$.	....	Tschirch and Oesterle.
Gurjunresene.... ...	Gurjun balsam...	$C_{17}H_{28}O_2$.	....	Tschirch and Weil.
Myroxoresene........	Fruit of myroxylons.	$C_7H_{10}O$.	....	Tschirch and Germann.
α-Masticoresene	Mastic..........	$C_{35}H_{56}O_4$.	74 to 75	Tschirch and Reutter.
β-Masticoresene.....	Mastic..........	....	....	Tschirch and Reutter.
Olibanoresene........	Olibanum.......	$(C_{14}H_{22}O)n$.	62	Tschirch and Halbey.
α-Panaxresene......	Burseraceous opopanax.	$C_{32}H_{54}O_4$.	....	Tschirch and Baur.
β-Panaxresene.......	Burseraceous opopanax.	$C_{32}H_{52}O_5$.	....	Tschirch and Baur.

GENERAL CHARACTERS OF RESINS.

The resins as a class are solid, more or less transparent, brittle sub-
stances, and in some cases are capable of crystallising. They have
usually no marked odour or taste, and vary in sp. gr. from 0.90 to 1.25.
The resins are easily fusible, but not volatile, and are decomposed
when heated in close vessels, yielding empyreumatic products consist-
ing chiefly of hydrocarbons. Heated in the air, the resins inflame
readily and burn with a smoky flame. They are very bad conductors
of electricity, and when rubbed become negatively electrified.

The resins are insoluble in water, but are soluble to a great extent in
alcohol and many other organic solvents. In most cases the solutions
are acid, to an extent depending on the nature of the resin, and when
treated with an alkali yield a lather. The solutions of the resins in
alkalies differ from ordinary soap solutions in the fact that they cannot
be "salted out" by the addition of common salt, unless this be used in
very large quantity.

Commercial Resins.

Many of the resins are important articles of commerce. A number
of them are used to an enormous extent for the manufacture of var-
nishes and in certain branches of soap-making. They are also em-
ployed in the manufacture of sealing-wax, for hat-stiffening, for in-
cense, and to a certain extent in medicine.

In the examination of resins, the following general principles should
be observed. Frequently it is not necessary to examine a resin in so
full a manner as the following processes involve, but in many cases
nothing but a full examination will give reliable information as to the
purity of the product.

Water and certain *general impurities* may be separated from the
resins by dissolving them in oil of turpentine, or other suitable solvent.
If the operation be conducted in a graduated tube, the separated water
may be measured and the insoluble matter filtered off, washed with
the solvent, dried, weighed, and further examined. The residue thus
obtained will often, especially in the case of medicinal resins, be found
to consist of woody fibre.

From the *neutral fixed oils* resins may be separated by treating the
mixture with alcohol of about 0.85 sp. gr. The alcohol is subse-
quently separated, and the dissolved resin recovered by evaporating

it to dryness. The results are only approximately correct. Acid resins, such as common colophony, may be separated from the neutral fats by boiling the substance with a strong solution of sodium hydrogen carbonate or borax. After cooling, the aqueous liquid is separated from the oil, and the resin precipitated from its solution by adding hydrochloric acid. Methods of separating resin from fatty acids are described under "Colophony."

Resins may be separated from the *essential oils* and *camphors*, in admixture with which they so frequently occur, by distilling the substance in a current of steam, and then, if necessary, immersing the flask or retort in a calcium chloride bath, while still continuing the current of steam.

Essential oils and camphors may also be separated by rubbing down the resinous substance to a fine powder in admixture with a known quantity of sand, and then macerating in petroleum-spirit. Part of the true resin will also be dissolved, and hence the filtered solution must be evaporated to dryness, the residue heated to 110° or 120° until constant in weight, and the weight found added to that of the undissolved portion, when the loss will be the essential oil and other volatile constituents. The amount of resin dissolved by the petroleum-spirit is often of interest. Thus, in the case of copal, the quality of the sample is better, the smaller the quantity of non-volatile matter dissolved by the petroleum-spirit. The mixture of ethereal oil and resin left on evaporating the petroleum-spirit at the ordinary temperature often yields more or less characteristic colour-reactions with the reagents for essential oils.

The residue insoluble in petroleum-spirit should be weighed and then treated with either, after which it should be ascertained if alcohol will extract anything insoluble in either or petroleum-spirit. In the case of gum-resigns, *sugar* is one of the principal substances extracted by alcohol, while gum, salts, etc., may subsequently be dissolved out by water, which in some cases (*e. g.*, gum tragacanth) may produce swelling without actual solution of the gummy matter. The ethereal solution should be tested as to its miscibility with alcohol, and a portion may be evaporated to dryness and the residue examined by colour-tests. It is also desirable to ascertain if a turbidity is produced by adding ether, ammonia, or an alcoholic solution of lead acetate to the spirituous solution of the original resin.

Mauch recommends the treatment of the substance with about 15

times its weight of a 60% solution of chloral hydrate in water. The liquor is filtered from woody fibre or other insoluble matter and the filtrate mixed with 10 parts of alcohol of 95%. This precipitates the gummy matters in a convenient condition for filtration and weighing, while the resinous matters and essential oils remain in solution.

Useful information may also be obtained by treating the original resin with chloroform, ether, or a saturated equeous solution of sodium carbonate; the last may produce colourations or dissolve out cinnamic acid and acid resins.

Various observers have applied to resins the methods which have been found so valuable in the examination of fatty and essential oils, and the acid values, saponification values, ester values, etc., have been determined. Karl Dieterich has devoted much time and attention to the investigation of this subject. The resins are complex substances, consequently their detection and analysis are of extreme difficulty. One general method equally applicable to all classes of resins cannot be adopted, and selected methods suitable for the material under examination must be applied.

Acid Value.—*a.* Direct titration in alcoholic solution with alcoholic potassium hydroxide.

b. For certain resins free from esters Dieterich has proposed his so-called indirect method. The resin is allowed to stand for 24 hours with excess of alkali, and is then titrated back with standard sulphuric acid. Although this cannot be considered a true acid value it has been found to give constant results, and can be considered as a legitimate method for determining a certain constant value.

c. Marcusson and Winterfeld have recently proposed a new method for estimating the acid value. The resin is boiled with a solvent containing equal parts of absolute alcohol and benzene. They have found this a very suitable method for determining the acid value of all the copals, dammar, sandarac, etc., and have obtained the following results:

Resin	Acid value	Resin	Acid value
Zanzibar copal	72.4	Amber (spurious)	14.5
Kaure copal	65.6	Mastic	60.2
Mania copal	141.8	Sandarac	137.7
Amber (mined)	26.7	Dammar	24.8
Amber (beach)	33.1	Elemi (soft)	15.2

Saponification Value.—This number can be determined in the ordinary way. Dieterich has also used hot, cold, and fractional saponification, but these values have as yet practically no value for commercial analysis. The *acetyl number* (Dieterich, H. A., 1897, 35) of resins (having the same significance as in the analysis of fatty oils) has occasionally been determined, as have the *carboxyl numbers*. (Kitt, Chem. Ztg. 1898, 358).

The table on page 15 gives the results obtained by G. Gregor and by Bamberger for the *methoxyl-number* (*Oest. Chem. Zeit.*, 1898, Nos. 8 and 9) of various resins and balsams. Gregor's modification of Zeisel's method was employed in each case. These figures have as yet only a limited value analytically.

The following table shows the figures recorded by Rowland Williams (R. W., *Chem. News*, 1888, **58,** 224); A. Kremel (K., *Pharm. Jour.*, 1887, **17,** 546); E. Dieterich and K. Dieterich (E. D., K. D., *Pharm. Jour.*, 1887, **17,** 546); von Schmidt and Erban (S. and E., *J. Soc. Chem. Ind.*, 1889, **8,** 308) and others.[1]

The acid and ester numbers in the table (p. 12) represent the numbers of milligrammes of KOH absorbed by 1 grm. of the sample, and were obtained in the usual manner, except in the case of the gum-resins, when the titration was effected in the following way (A. Kremel; E. and K. Dieterich):

1 grm. of the gum-resin was mixed with powdered gypsum and extracted with 95% alcohol. The residue from the evaporation of the alcoholic extract (which gives the percentage of resin) was then redissolved in 50 c.c. of alcohol, one-half of the liquid being used for the acid determination and the other half for the esters. The amount of KOH used was then calculated to 1 grm. of the pure resin. The method followed by von Schmidt and Erban for the estimation of the amount of iodine absorbed was to dissolve 1 grm. of the resin in hot alcohol, when, after cooling the liquid, the iodine solution was added in excess. The mixture was allowed to stand for twenty-four hours before titration. The figures in the table marked with an asterisk were obtained on that portion of the resin soluble in alcohol, the insoluble matter being separated. The remaining iodine-absorption figures of von Schmidt and Erban (not marked by an asterisk) were obtained on the alcoholic solution in presence of the insoluble residue.

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[1] The figures for *shellac* have been omitted from the table, since most of the samples examined were obviously adulterated. All the reliable data with reference to this resin will be found on pages 70 *et seq.*

The figures in the table on page 14, obtained by the analysis of resins used in the manufacture of spirit-varnishes, are due to A. Rudling (Chem. Rev. Fett. u Harz. Ind., 1903, **10**, 51). Those referring to shellac are omitted owing to the obvious impurity of some of the samples examined. The figures in columns A were obtained with the crude resins; in B with the dry samples after being freed from mechanical impurities. Columns C refer to the alcoholic extract after drying at 100°.[1]

The foregoing methods afford valuable indications of the nature of resinous substances, but the positive identification of the various individual resins of commerce is a matter of considerable difficulty even when only one is present, and in admixture the task is often insuperable.

This conclusion is emphasised by the fact that in the manufacture of varnishes, the resins are usually heated together with oil or other substances to a temperature of about 300°. The effect of such heating is exemplified by various figures given by J. Lewkowitsch (*Analyst*, 1901, **26**, 38). From his results it appears that not only do different commercial samples of presumably similar nature and origin give very varying figures, but the effect of heat on a given sample is often such as to destroy any analytical characters it previously possessed. It is desirable to place the results on record, but it is evident that at present any conclusion as to the origin or purity of a resin, from the figures obtained by its analysis, must be drawn with the greatest caution.

[1] In these analyses, the iodine value was estimated by dissolving 0.5 to 1.0 grm. in 25 c.c. of alcohol with 10 c.c. of chloroform, and titrating after 6 hours. The saponification value was estimated by boiling 1 grm. of the resin for 15 mins. with 25 c.c. of potassium hydroxide solution under a reflux condenser, then diluting the liquid with 100 c.c. of alcohol, and titrating with standard acid; and the acid value by boiling 1 grm. of resin for 5 mins. under a reflux condenser with 100 c.c. of 90% alcohol, and titrating the liquid when cold.

ANALYTICAL CONSTANTS OF RESINS.

Substance	Source or variety.	Acid number	Ester number	Iodine absorption	Ash	Observers.
				%	%	
Resins.						
Amber	*Pinus Succinifer*	15	71	62.1	0.28	R. W.
Anime	Various	33; 34	74; 91			K.
Caoutchouc		18 to 27	47 to 62	128 to 137	0.05 to 0.11	R. W.
Colophony	Residue from turpentine distillations. *Pinus* species	81		71		S. & E.
	Refined	146	22	116.8*		S. & E.
	Ordinary	179; 178	8; 18	115.3; 114.8	0.05; 0.02	R. W.
	Various	169; 167	7; 23	112.0; 113.3	0.08; 1.20	R. W.
Copal	*Trachylobium* and *Hymenza* species	151 to 173				S. & E.
	Various	30; 94	25; 89	34.8; 44.9		
	Various	80 to 147		122 to 142	trace to 2.06	R. W.
	Various	46 to 141	35 to 85			Lippert and Reissiger.
		59 to 148				
Copal (Kauri)	*Dammara Australis*	52 to 63	26 to 36	151 to 164	0.08 to 0.12	R. W.
Dammar	*Dammara* and *Hopea* species	33	14	63.6	0.03 to 0.07	S. & E.
	Batavia	21 to 27	4 to 20	130 to 142	0.01	R. W.
	Various	15 to 34	14	117.7		R. W.
Dragon's Blood	*Dæmonorops Draco* and *Dracæna Cinnabari*	11	142	98.4	3.58	R. W.
				72.4		S. & E.
Elemi	*Bursera* species	22	3	85.1*		S. & E.
	Manila	16; 18	13; 8	175.4	0.04	R. W.; K.
Guaiacum	*Guaiacum officinale*	3	24			K.
Jalap	*Ipomæa purga*	23 to 44				K.
Jalapin	Jalap resin	12; 13	140; 121			K.
		15	173	159		R. W.
Mastic	*Pistacia lentiscus*	50 to 56	23		0.14 to 0.20	K.
		62; 71				
		64	29	64.4		S. & E.

ANALYTICAL CONSTANTS OF RESINS—CONTINUED.

Substance	Source or variety	Acid number	Ester number	Iodine absorption	Ash	Observers
Sandarac...	Callitris quadrivalvis...	146 to 154 / 141	1 to 11 / 33	0134.3 / 66.8*	0.04 to 0.17	R. W. / S. & E.
Oleo-resins.[1]						
Canada balsam...	Abies balsamea...	81 to 87	4.5 to 9.0			K.; E. D. / P. Dietze.
Copaiba balsam...	(See table on page 87.)					
Gurjun balsam...		5.8 to 20	11.3 to 11.2			K.; E. D.
Mecca balsam...	Balsamodendron gileadense	40 to 52	101.4			K.; E. D.
Common turpentine...	Pinus Sylvestris, P. Cembra,					
Chian turpentine...	Abies species, etc...	108 to 145	3 to 60.2			K.; E. D. / R.; E. D.
Venice turpentine.		48; 53 / 68; 70	19 to 21.50			E. D. / S. K.
Burgundy pitch...		142	32	149.3*		
Gum-resins.						
Ammoniacum...	Dorema Ammoniacum.					K.
	African...					K.; E. D.
	Persian...	59	123			K.; E. D.
Asafœtida...	Ferula species...	57 to 135	31 to 98			K. D.
Bdellium...	Various Burseraceæ	11 to 82	82 to 182			Beckurts &
Euphorbium...	Euphorbia resinifera.	10 to 37 / 13 to 25	47 to 96 / 49 to 68			Bruche: K.
Galbanum...	Peucedanum species.	5 to 69 / 81 / 100	55 to 179 / 67 / 57	115.8		E. D. / R. W.
Gamboge...	Garcinia Morella...				0.48	K.
Myrrh...	Herabol-Myrrh...	64 to 70 / 25 / 42	95 to 146 / 204 / 131			K. D. / K.
Olibanum...	Indian...	45 to 88 / 50	7 to 72 / 60			K.; E. D. / K.
	Boswellia species...					
	Indian...					

[1] Whilst retaining the ordinary names for certain oleo-resins, it may be again pointed out that these substances here treated are not true balsams, these substances having been already discussed under the aromatic acids, since their chief characteristic is the presence of the acids with resinous substances.

ANALYTICAL CONSTANTS OF RESINS (A. Rudling).

Resin	Water	Substance insoluble in alcohol	Iodine value			Saponification value			Acid value		
			A	B	C	A	B	C	A	B	C
	%	%									
Yellow acaroid (xanthorrhea) resin	5.65	0.93	176.2	188.6	160.0	98.0	104.9	106.0	82.3	88.1	64.0
Yellow acaroid resin (Adelaide)	4.50	3.52	176.2	191.5	160.0	100.8	109.5	106.0	67.2	73.0	67.0
Yellow acaroid resin (Victoria)	4.40	0.88	175.0	184.7	160.0	146.8	165.5	176.4	72.8	76.8	84.0
Red acaroid resin	4.90	5.26	164.5	183.1	136.7	64.4	71.7	106.0	18.5	20.6	25.0
Sandarac	2.00	0.54	91.8	94.2	98.7	152.4	166.7	170.8	137.2	140.8	127.8
Manila (spirit soluble)	2.10	2.30	106.0	110.8	91.0	187.6	196.2	187.6	136.6	142.8	150.0
Manila (hard)	1.68	3.39	86.0	90.6	.....	215.6	227.1	.....	138.9	146.3	.....
White French resin	0.80	0.10	137.1	138.3	.....	177.8	179.4	.....	169.7	171.2	.....
American resin	0.75	0.20	122.0	123.2	.....	182.0	183.8	.....	157.9	159.4	.....
Venetian turpentine (genuine)	.....	.....	148.5	.....	.....	121.8	.....	.....	73.9	.....	.....
Venetian turpentine (spurious)	.....	.....	109.6	.....	.....	117.6	.....	.....	103.9	.....	.....
Elemi	0.2	0.1	83.6	83.8	.....	28.0	28.0	.....	22.4	22.4	.....

METHOXYL-VALUES OF RESINS.

No.	Description of resin or balsam	Methoxyl-number			
		Gregor		Bamberger	
1	Aloë hepatica.....	4.2		3.9	
2	Aloë lucida.....	0		0	
3	} Ammoniacum....	8.6	..	11	
4		9	.		
5	} Asafœtida.....	11.0		18	
6		6.9	..	.	
7	Gum benzoin, Siam...	43.4	4.3	30	28.5
8	}	25.5	25.3	16.5	16.2
9	} Gum benzoin, Sumatra....	20.3	..		
10		20.1	..		
11	Benzoin (almond), Sumatra	20	..	13.3	
12	Canada balsam.....	0	..	0	
13	Copaiba balsam....	0	.	0	
14	Copal........	0	..	0	
15	Colophony........	0	..	0	
16	Dammar.....	0	..	0	
17	} Dragon's blood.	27.6	..	33.8	
18		25.3	..	..	
19	} Euphorbium.	0	..	0	
20		2.8	..	0	
21	} Elemi.....	0	..	0	
22		2.5	..	..	
23	Pine resin....	0	..	0	
24	Galbanum.....	3.7	..	3.7	4
25	} Gamboge......	0	..	0	
26		2.4	..	..	
27	Guaiacum.....	73.8	74.2	83.8	84.0
28	Gurjun balsam....	0	..	..	
29	Jalap resin.....	0	..	0	
30	Labdanum....	0	..	0	
31	} Liquidambar styrax.....	4.5	..	0	
32		3.6	..	..	
33	Myrrh.........	13.5	..	13.6	13.2
34	} Gum mastic......	0	..	0	
35		1.9	..	..	
36	Olibanum......	6.4	..	5.3	
37	}	16.7	..	14.4	
38	} Balsam of Peru...	21.8	21.7	..	
39		22.6	..	..	
40	Scammonium....	0	..	0	
41	Sandarac......	0	..	0	
42	Venice turpentine.....	0	..	0	
43	} Balsam of Tolu.....	41.6	..	46.8	
44		41.7	..	..	

RESINS.

ACAROID RESINS.

Occurrence.—Red and yellow acaroid resins are the products of various species of Xanthorrhœa, especially of *X. australis*, plants found over a wide area of the Australian continent. In addition to the Australian gums, a red West Indian variety is also known.

Chemical Composition.—According to K. Hildebrand, the composition of red and yellow acaroid resins is very similar, the main distinction being the presence of cinnamic acid in the latter kind. In the red resin, which is chiefly the product of *X. australis*, he found 1% of free *p*-coumaric acid, and 2% of this acid as an ester of erythro-resinotannol, $C_{40}H_{39}O_9.OH$; traces of benzoic acid also in combination; and traces of *p*-hydroxybenzaldehyde. About 85% of the resin consists of the *p*-coumaric acid ester and the resin alcohol. The yellow resin contains about 4% of free *p*-coumaric acid and a small quantity of free cinnamic acid. Both acids, chiefly the former, are present in the form of esters of xantho-resinotannol, $C_{43}H_{45}O_9.OH$, and these substances form the principal portion of the resin. In addition, traces of several compounds which have not been definitely identified are also present. These probably consist of styracin, phenyl-propylcinnamate, *p*-hydroxybenzaldehyde, and vanillin.

Uses.—These resins are used in the manufacture of sealing-wax, the preparation of spirit lacquers for coating metals, especially the brass parts of scientific instruments, to a small extent in medicine, and the darker varieties when dissolved in alcohol, make an excellent mahogany stain for wood. The acaroid resins when dissolved are fast to light, consequently they are in some cases preferable to dragon's blood as colouring media. The alkaline solutions of these resins can be used for sizing paper.

Adulterants.—Owing to the low price at which these resins are sold, they are not adulterated, but are frequently used to adulterate the more expensive resins.

General Properties.—Yellow acaroid resin occurs mostly in long or round pieces of a red-brown colour, which possess an odour resembling that of benzoin.

Red acaroid resin (Australian), the so-called "grass-tree gum," is found in large and small uneven pieces of a brownish colour, often

nixed with sand and other impurities; thin pieces when examined by
transmitted light show a ruby-red colour. It differs from yellow
acaroid, or "Botany Bay gum," in not giving a cinnamic acid reaction.
According to Maiden, only about 2% of the yellow acaroid resin is
soluble in petroleum ether, and as much as 90 to 95% in alcohol. Red
acaroid resin, however, yields as much as 3% to petroleum ether.

Red Acaroid Resin (West Indian).—This resin from the Bahamas
presents the appearance and character of the red commercial variety.
It is light in colour, quite soluble in alcohol, and yields only about 3%
of ash. The composition appears to agree very closely with that of
the Australian resin, although, unlike the latter, it yields cinnamic acid
on treatment with alkaline solutions. West Indian acaroid can be
used for the same purpose as the Australian varieties, except that its
light colour would preclude its use as a stain.

Identification and Analytical Data.—H. Rebs (*Lack- und Farben-
Ind.*, 1908, No. 11) has described the following method for identifying
acaroid resin in the presence of manila, shellac, sandarac, and coloph-
ony. A small amount of the material under examination is heated
with 10 to 20 drops of nitric acid until nitrous fumes are copiously
evolved. When cold, the residue is dissolved in alcohol, and 10 to
20 drops of a 5% ferric chloride solution are added to the intensely red
liquid. A brown to brownish-black coloration accompanied by a
cloudy appearance in the liquid, denotes the presence of gum acaroid.
By this means 1% can easily be detected.

Schimmel & Co. give 4.9 as the acid number and 69.4 as the ester
number of a sample of yellow resin. Rudling examined various sam-
ples of these resins, and the numbers obtained by him are given on page
14. An essential oil distilled from yellow acaroid obtained from
X. hastile was an oil of storax-like odour having a sp. gr. of 0.937 and
an optical rotation of —3.25. The saponification number of the oil
was 74.3, and the acid number 4.9, showing the presence of a large
proportion of esters. The free acid was identified as cinnamic acid
which was also found in the esters. From the low boiling fraction
styrene was isolated.

Haensel (*Apoth, Zeit.*, 1908, 23, 279) has described acaroid resin
oil as an optically inactive reddish-brown liquid with an odour recalling
Tolu balsam. It has a sp. gr. 0.960, an acid value 47.6, and ester
value 37.5. When treated with a solution of sodium hydroxide, 1.94%
of cinnamic acid and 7.6% of a yellowish resin are removed. The

washed oil when saponified gives a furtner yield of cinnamic acid and
resin.   Styrene is also present in the oil.

AMBER.

Occurrence.—Amber is a fossil resin derived from *Pinites succinifer.*

Commercial Varieties.—A number of varieties are known com-
mercially, but, according to Helm and Potonic (*Ph. C.*, 1890, 744),
the following kinds should be regarded as distinct:

1. Succinite, the most important variety, and the one that is gen-
erally specified under the name amber, forms yellow or yellowish-brown
masses which are often quite transparent or semi-transparent, but
sometimes so milky as to be quite opaque.

2. Gedanite, also known as "soft amber," is a pure yellow, trans-
parent variety which swells at 140° to 180° and melts on further heating.
It is said to contain less succinic acid than ordinary amber.

3. Glessite, usually brown and opaque.

4. Stantienite or black resin, a brittle variety.

5. Beckerite, a brown opaque resin.

Imitation Amber.—This product is manufactured to a certain ex-
tent from the shavings of amber produced when the pieces are trimmed.
Very strong pressure is used, and although the resin is all genuine
amber, the peculiar method of aggregation of its particles causes it to
differ in its physical properties from natural amber, so that the term
"spurious amber" appears to be justifiable.   Sometimes, however,
colophony and others resins are worked in.

Chemical Composition.—According to Tschirch and Aweng,
amber contains 2% of the bornyl ester of succino-abietic acid; 28% of
free succino-abietic acid,[1] $C_{80}H_{120}O_8$; and 70% of the succino-resinol
ester of succinic acid.   From the last-named substances they isolated
the free *succino-resinol,* $C_{12}H_{20}O$, as a white powder melting at 275°,
and possessing the usual characters of a resin alcohol.

Small quantities of sulphur are present in most varieties of amber.
Gedanite is said to be free from this element, although its main con-
stituents are identical with those of ordinary succinite.   Glessite differs
from succinite in the absence of the bornyl radical, which is replaced
by the carvyl group.   Free succinic acid is stated by P. Dahms to be

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[1] On treatment with alcoholic potassium hydroxide succino-abietic acid is decomposed
with formation of a dibasic alcohol, *succino-abietol,* $C_{40}H_{60}O_2$, and *succino-sylvic acid,*
$C_{24}H_{36}O_2$.

"present in amber in proportions ranging from 3 to 8%, but its presence is denied by other observers.

Uses.—This gum is at present largely employed for the manufacture of ornamental articles. It is also used in the artificial silk industry to increase the elasticity of the finished article. Formerly the darker ambers were used in the varnish industry, but this resin is now very expensive, and in addition there are difficulties in the manufacture which make the resulting varnish too dark for ordinary use. The general public still considers amber varnish as the best commercial variety, but in trade circles it is known that only very small quantities of the varnish sold under this name really contain amber.

Adulterants.—Soft copals, specially prepared rosin, and the amber-coloured fluorides are frequently used as adulterants, and it is imitated artificially by coloured glass and celluloid. The imitation amber previously mentioned is also sold in place of the genuine article.

General Properties.—Amber varies in colour, transparency, and translucency. Often the same sample shows marked variations in this respect. The colour varies from pale yellow, through shades of dark yellow and brown, to black. Some specimens are transparent, others are opaque, while intermediate varieties—the cloudy ambers—are also found. Amber is a hard, brittle substance which breaks with a conchoidal fracture. It is the hardest known resin, and in the terms of Mohr's scale has a hardness from 2 to 2.25. The fused resin gives a slightly lower figure. When rubbed, it polishes readily, and at the same time becomes negatively electrified, emitting an odour which is characteristic for the resin.

Specific Gravity.—1.08 may be taken as an average figure, but the gravities of different samples vary from 1.050 to 1.096.

Melting-point.—When heated to 287° amber melts with decomposition, and when the heating is continued water, succinic acid, small amounts of volatile fatty acids, and a camphor-like substance together with oil of amber are given off, leaving a residue which is completely soluble in turpentine and drying oils.

Solubility.—Amber is soluble only to a small extent in most of the usual organic solvents. Dichlorhydrin is one of its best solvents. In alcohol, methyl alcohol, petroleum-ether, and acetone, amber is practically insoluble either before or after melting, and in acetic acid, ether, amyl alcohol, benzene, and chloroform before melting, when it is partially soluble in carbon disulphide and oil of turpentine.

Amber after melting is partially soluble in ether, amyl alcohol, acetic acid, and chloroform, and almost entirely soluble in benzene, carbon disulphide, and oil of turpentine.

Analytical Data.—The following analytical characters of genuine amber have been recorded:

	R. Williams	A. Kremel
Water, %.....................	1.05	
Ash, %......................	0.28	
Acid number.................	15.4	33.4 to 34.4
Ester number...............	71.4	74.5 to 91.1
	0	

A sample of natural amber having a total saponification-number of 144.8, was found by von Schmidt and Erban to give the figure 36 after melting, thus showing that this process resulted in the destruction of the greater part of the esters.

Detection of Adulterants.—1. Imitation amber. Genuine amber is double refracting, and when viewed by polarised light (with crossed Nicol prisms) it shows only very faint colours, whereas the want of homogeneity of the pressed article causes it to exhibit brilliant inter-ference tints.

2. Soft copals. *a.* Cajeput oil dissolves the copals, whereas amber is insoluble in this medium. *b.* Amber when held in a Bunsen flame burns without melting. *c.* Amber has a high ester value; esters are not present in the copals. *d.* When warmed with potassium hydroxide solution, copals give off the characteristic odour of copaiba balsam. *e.* Rossler states that amber when heated in a hard-glass tube evolves sulphurous fumes which blacken lead acetate paper. Copals from all sources give negative results when subjected to this test.

3. Hard copals. Amber can be differentiated from the hard copals by testing the hardness. Livache gives the following method: Take a crystal of rock salt and obtain a polished face by cleavage. Examine the suspected samples by driving a sharp corner of each across the crystal of rock salt, then examine the latter under a magnifying glass. Amber leaves a scratch on the surface of the crystal, but the hard copals are too soft to effect this result.

4. Colophony. *a.* The presence of colophony considerably increases the acid value of the sample. *b.* Solubility in alcohol. *c.* When boiled in water colophony softens. *d.* Pure amber when spotted

with alcohol is unaffected, but a dull spot remains on samples which have been adulterated with colophony.

5. Fluorides, hardened rosin, etc. Attention would be called to these adulterants by the high ash value. The presence of a large percentage of alkaline earth oxides would lead the analyst to suspect hardened rosin as the impurity.

6. Celluloid. Rubbing develops an odour of camphor. It is not electrified appreciably on rubbing. Saponification with alcoholic potassium hydroxide separates the NO_3 radical and cellulose.

Oil of amber (*Oleum succini*), obtained by destructive distillation of amber, has a limited use in medicine. Authentic samples of amber oil examined by E. J. Parry had a sp. gr. of about 0.950 and an optical rotation of about $+15°$. According to Schimmel & Co. (*Semi-Annual Report*, April, 1903), the pure oil differs markedly from the commercial article, the optical rotation of the former ranging from $+22.5°$ to $+26°$, and that of the commercial oils from $-2°$ to $+13°$. There is no doubt that commercial oil of amber is almost entirely distilled from cheap resins other than amber.

COLOPHONY. COMMON ROSIN.

Common rosin, or colophony, is the fixed residue obtained by the distillation of the turpentine or oleo-resin obtained from various species of pine, but chiefly from *Pinus australis, P. tæda, P. pinaster*, and *P. laricio*.[1]

Commercial Varieties.—French and American rosins are the two chief commercial varieties. The former comes on to the market under the name of galipot, while the various grades of American rosin are designated by letters. For instance grade A is almost black, other letters denote increasing paleness until W. G. is the so-called "water glass" and W. W. "water white" rosin.

Chemical Composition.—Colophony consists chiefly of an acid together with small quantities of isomeric or polymeric inert substances and traces of mineral constituents and bitter principles. The unsaponifiable substances are probably composed of hydrocarbons, similar to those contained in rosin oil, produced by the action of heat on the

[1] After distillation of the essential oil the melted resin is removed from the stills and run through wire strainers into barrels. The lightest-coloured rosin is obtained from trees which have been tapped for the first time, and it then constitutes about 80% of the oleo-resin. In subsequent years the proportion of resin in the crude turpentine gradually increases, and the resin from a given tree also becomes darker year after year.

colophony during the process of manufacture. The chemistry of colophony has been the subject of various researches with curiously conflicting results. According to Maly, the principal constituent of colophony is abietic anhydride, but this statement is at variance with the ready manner in which colophony reacts with alkalies. Mach obtained abietic acid from colophony by a preliminary treatment with 70% alcohol, and crystallisation of the insoluble portion from 90% alcohol. After 30 crystallisations a pure white substance was obtained which began to soften at 148° and melted when slowly heated at 153° to 154°. As the result of combustion experiments supported by cryoscopic and ebullioscopic determinations, he assigns a formula, $C_{19}H_{28}O_2$, to the acid and puts forward the view that abietic acid, sylvic acid, and pimaric acid are identical. Tschirch and Studer (*Arch. Pharm.*, 1903, **241**, 495) accept the above formula as correct, although their analyses, even taking into consideration the probability of oxidation, do not agree with the suggested formula.

W. Fahrion investigated samples of American rosin; he found it to consist chiefly of an acid which he calls sylvic acid. This exists in colophony in an amorphous form, which on treatment with dilute alcohol or when acted on in alcoholic solution with hydrochloric acid gas is converted into a crystallisable modification, which melts at a higher temperature, and is reconverted into the amorphous form by prolonged heating; secondary products are also produced. The m. p. of abietic acid is very variously stated, Mach giving it at 153° to 154°, Dragendorff at 144°, and others again as high as 165°. P. Levy (*Zeit. angew. Chem.*, 1905, **18**, 1739) has recently obtained from colophony, by vacuum distillation and crystallisation of the product many times from methyl alcohol, pure abietic acid with a m. p. of 182.° The elementary analysis and molecular weight determinations together with an examination of the derivatives has proved the correctness of the formula proposed by Bischoff and Nastvogel and accepted by Fahrion.[1]

[1] W. Fahrion adopts the formula $C_{20}H_{30}O_2$ for abietic (sylvic) acid, and confirms the following constitutional formula proposed by Bischoff and Nastvogel:

$$CH : C(CO_2H) . CH . CH . CMe_2 = CH$$
$$CH_2 . CHPr — CH . CH . CHPr . CH_2$$

(Pr = Propyl).
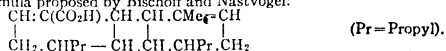
Fahrion has shown that abietic acid is very liable to spontaneous oxidation, and this is the cause of the low values for carbon and hydrogen obtained by certain other workers on this substance.

While agreeing in ascribing to pimaric acid the formula $C_{20}H_{30}O_2$, observers differ greatly as to its characters. According to A. Vesterberg (*Ber.*, 1885, **18**, 3331; 1886, **19**, 2167; 1887, **20**, 3248), two varieties of pimaric acid exist. *Dextropimaric acid* has a specific rotation in alcoholic solution of + 72.5°, melts at 210° to 211°, and distils in a vacuum almost unchanged and without formation of sylvic acid. Ammonium dextropimarate is said to separate in fine needles when an ethereal solution of the acid is agitated with ammonia. *Lævopimaric acid* is very strongly lævorotatory ($[a]_D = -272°$), and melts between 140°

When its alcoholic solution is slowly evaporated abietic acid is deposited in crystalline laminæ. Prolonged heating is stated to convert abietic acid into its anhydride.

Abietic acid is quite insoluble in water, but dissolves readily in strong alcohol, ether, chloroform, benzene, carbon disulphide, and glacial acetic acid. According to Mach, abietic acid dissolves in strong sulphuric acid with red colour.

According to W. Fahrion, abietic acid oxidises spontaneously with formation of *peroxides* containing $C_{20}H_{30}O_4$ and $C_{20}H_{30}O_6$. These substances are insoluble in petroleum-spirit, but undergo intramolecular change with formation of *dihydroxy-abietic* and *tetrahydroxy-abietic acids*, $C_{20}H_{29}(OH)O_3$ and $C_{20}H_{28}(OH)_2O_4$, which are soluble in petroleum spirit. The latter acid is also produced by the oxidation of abietic acid by permanganate in alkaline solution. Other indefinite products are also formed by the oxidation of abietic acid and occur in colophony.[1]

Abietic acid is frequently described as dibasic, but the presence of only one carboxyl-group in the molecule and the proportion of alkali required for its neutralisation conclusively negative this view. Abietic acid forms a series of salts, some of which are crystallisable. The abietates of the alkali-metals are readily soluble in water, alcohol, and ether, and are possessed of marked detergent properties. Hence the employment of rosin in soap-making. An acid potassium abietate, obtained by Mach by neutralising an alcoholic solution of abietic acid with alcoholic potash, or boiling it with potassium carbonate, forms bundles of silky needles melting at 183°. The normal potassium salt also crystallises in silky needles, while the barium salt is described as a white, amorphous compound, which becomes yellow on exposure to air.

According to Perrenoud, the ammonium salt of abietic acid from colophony is gelatinous, whereas the acid ammonium salt of pimaric acid crystallises in handsome needles.

Uses.—Colophony is employed very largely in the manufacture of soap, for the preparation of varnishes and resinate driers in the varnish

and 150°. S. Haller (*Ber.*, 1885, 18, 2165) describes pimaric acid as optically inactive and melting at 149°. Pimaric acid is said to differ from abietic acid in having a bitter taste.

[1] F. Jean (*Chem. News*, 1872, 26, 207) has described three acid resins as occurring in colophony. Resin A, probably identical with abietic acid, is insoluble in water, but soluble in alcohol, ether, and oil of turpentine. Resin B is insoluble in the last solvent, and is also distinguished from A by yielding a sodium salt insoluble in sodium hydroxide solution of 1.116 sp. gr. Resin C is soluble in water, and its aqueous solution is precipitated by silver and cupric salts. Tschirch and Studer claim to have isolated 3 isomeric abietic acids from American colophony. Two of the acids form insoluble lead salts (*Arch. der Pharm.*, 1903, 241, 495).

industry, to a certain extent in pharmacy, especially in veterinary
practice, and the soluble salts are now used in the paper industry for
sizing paper.   Large quantities of rosin are also employed in the
manufacture of rosin oil.

Adulterants.—Colophony is such a cheap material that it is very
rarely adulterated, but it is a favorite adulterant of the more expensive
resins, such as shellac, dammar, dragon's blood, guaiacum, storax,
benzoin, etc.

General Properties.—Colophony, or rosin, is a soft transparent or
translucent resin of a faint terebinthinate odour which is more notice-
able when the resin is held in the hand.   It is nearly tasteless, but
some varieties possess a nauseous and highly characteristic after-taste.
Colophony is very brittle, and shows a shallow conchoidal fracture
when broken.   It varies in colour from a very pale amber to a very
dark reddish-brown.   The darkest kind is known commercially as
black rosin.   Powdered rosin varies in colour from white to pale
yellow.

Specific Gravity.—The sp. gr. of this resin usually lies between
1.07 and 1.08.   Dieterich gives 1.045 to 1.086 as the limit figures
for good commercial samples.   This constant may be conveniently
ascertained by immersing small pieces of the resin free from air bubbles
and mechanical impurities in brine solutions of varying densities and
estimating the gravity of the solution in which they remain suspended.

Melting-point.—Colophony has no sharply defined m. p.   It softens
at a temperature of 70° to 80°, becomes semi-fluid in boiling water,
and melts completely at a somewhat higher temperature.   The final
point of fusion varies with different samples, but 135° should not be
exceeded.   When heated in the air colophony ignites and burns with
a yellow and very smoky flame, leaving a trifling quantity of ash.
When the flame is blown out a highly characteristic odour is noticeable.
On distillation colophony undergoes a complex decomposition with
the production of two important products, rosin spirit and rosin oil,
both of which are described elsewhere.

Solubility.—Colophony is quite insoluble in water, although it con-
tains small proportions of soluble substances.   At 60° it dissolves slowly
in an equal weight of alcohol or glacial acetic acid, and is also readily
dissolved by methyl and amyl alcohol, acetone, ether, chloroform,
carbon disulphide and the fixed and volatile oils.   Petroleum ether
does not dissolve colophony completely.   Dieterich put forward the

suggestion that not more than 7% of a good quality rosin should be insoluble in this medium, but experience has proved that the insoluble portion may vary from 1 to 20% in samples which are suitable for certain commercial purposes.

According to We Fahrion, colophony for use in varnish manufacture should be light in colour and have a high acid number approaching to that of sylvic acid, 185.4. The quantities of material insoluble in petroleum ether and the amount of unsaponifiable matter should be small.

Analytical Data.[1]—*a.* Ash, extremely small. *b.* Acid value. The acid number of colophony normally ranges between 155 and 175. This represents a proportion of resin acids in terms of $C_{20}H_{30}O_{2}$ ranging from 83.4 to 93.8%. Dieterich suggests the following method for the determination of its value:

About 1 grm. of the finely powdered material is suffused with 25 c.c. of alcoholic potassium hydroxide and left covered until the whole has dissolved. The excess of alkali is then titrated back with sulphuric acid. The number of c.c. of alcoholic potassium hydroxide required multiplied by 28.08 gives the acid value (indirect). It is extremely doubtful whether the above method offers any advantages. The continued action of the alkali may affect the substances other than true acids in the resin and falsify the results. Direct titration in alcoholic solution with alcoholic potassium hydroxide can be strongly recommended to give constant results. *c.* Ether value. In addition to the free acid number obtained by direct titration of the resin in alcoholic solution with alkali hydroxides and phenolphthalein, colophony neutralises a small additional quantity of alkali on complete saponification. This additional neutralising power was at first thought to be due to the presence of resin esters, but R. Heinriques (*Chem. Rev. Fett- Harz-Ind.*, 1899, **6**, 111) has proved the absence of these. Probably the hydrolysis of abietic anhydride or lactone acids causes the extra quantity of alkali to be neutralised. This value varies considerably in different samples of rosin and can scarcely be used as a means of identification.

[1] K. Dieterich has suggested that rosin should pass the following standard tests: It should be as light coloured as possible, and when boiled with water the extract should, when tested with ferric chloride solution, give a minimum colour reaction. In alcohol, ethereal oils, acetone, ether, chloroform, methyl alcohol, amyl alcohol, acetic ether, benzol, oil of turpentine, and carbon disulphide it should be completely soluble, and partly soluble in benzin and petroleum ether.
   The acid value when indirectly determined should only vary between 145 and 185. The quantity of ash should be small.

The following table shows the acid and saponification numbers recorded for various samples of commercial rosin. The ester numbers are the differences between the two former figures.

Kind of rosin	Acid number	Ester number	Saponification No.	Observer	Reference
American (6 samples)	154.1 to 164.6	15.7 to 30.0	174.7 to 194.3	J. Lewkowitsch	J. Soc. Chem. Ind., 1893, 12, 505.
Austrian	146.0	21.1	167.1	v.Schmidt & Erban	J. Soc. Chem. Ind., 1889, 8, 308.
Typical (6 samples)	154.0 to 162.0	14.4 to 19.8	174.3 to 177.6	Smetham & Dodd	J. Soc. Chem. Ind., 1900, 19, 102.
White	172	7.0	179	H. Amsel	Zeits. ang. Chem., 1896, 9, 429.
Yellow; new	162	7.0	169	H. Amsel	Ibid.
Yellow; old	167	8.0	175	H. Amsel	Ibid.
Very pale	155	12	167	A. H. Allen	Unpublished note.

In addition to the above data, A. Kremel (*Pharm. Jour.*, 1887, [3], 17, 547) found acid values varying from 151.1 in dark Austrian colophony to 173.6 in an American specimen. Beckurts and Brüche have recorded 180, 181, and 185 as the acid values of samples of white, brown, and yellow rosin, respectively, and give identical figures for the saponification values of the same samples, a result which is improbable. In red rosin they found acid values ranging from 173 to 186, with saponification numbers from 179 to 193. R. Williams has published the results yielded by four samples of rosin (*Chem. News*, 58, 224), but the figures are admittedly abnormal.

Two samples of American colophony analysed in Allen's laboratory (1903) by S. O. Richmond gave the following results:

	Pale	Brown
Sp. gr	1.069	1.081
Acid number (by titration with aqueous alkali, A)	157.9	172.4
Acid number (by titration with alcoholic alkali, a)	154.0	168.4
Total saponification number (B)	169.4	176.2
Ester number (B—A)	11.5	3.8
Ester number (B—a)	15.4	7.8
Unsaponifiable matter, %	9.25 } 9.93 }	4.28

It will be observed that the figures obtained by dissolving the sample in strong alcohol, and titrating the solution with alcoholic alkali hydroxides, are somewhat lower than those obtained when seminormal

aqueous sodium hydroxide was employed for the titration, but the
differences are not great. As the total saponification number was
determined by titrating back the alcoholic alkaline liquid with aqueous
hydrochloric acid, the figures for free acid obtained by titration with
aqueous alkali have been used in calculating the following composition
of the samples from the data recorded above:

	Pale	Brown
Abietic acid ($C_{20}H_{30}O_2$)	85.16%	92.96%
Abietic anhydride ($C_{40}H_{58}O_3$)	6.04%	1.99%
Hydrocarbons (unsaponifiable matter)	9.25%	4.28%
	100.45	99.23

These results show that the samples examined consisted chiefly
of abietic acid, and did not contain any large proportion of abietic
anhydride or lactone acids. The unsaponifiable matter was of a very
pale straw-yellow colour. That from the pale rosin was soft and
"tacky," but that from the brown sample was somewhat harder.

The sample of pale rosin described above was also examined by
Tschirch's process (page 2) with the following results:

		%	Combining weight
Resin acids	Soluble in 1% ammonium carbonate solution	2.62	326.6
	Soluble in 1% sodium carbonate solution	88.62	343.9
	Soluble in 1% sodium hydroxide solution	0.64	
Unsaponifiable matter	Volatile with steam (terpenes)	1.00 }	7.05[1]
	Not volatile with steam	6.05 }	
		98.93	

The original sample of pale rosin, and the separated resin acids and
unsaponifiable matter, all gave a fine purple coloration, fading slowly
to brown, when they were dissolved in a little acetic anhydride, and a
drop of sulphuric acid (sp. gr. 1.53) added. When dissolved in acetic
anhydride and a drop of stannic tetrabromide added, a purple colora-
tion was produced in each case, the colour fading slowly to dark brown.

Unsaponifiable Matter.—Holde und Marcusson (*Mittheil. Königl.
tech Versuchsanstalt.*, 1902, 40) state the average amount of unsa-

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[1] It will be observed that the proportion of unsaponifiable matter isolated is materially
less than that previously found.

ponifiable matter in colophony as 8%. The highest recorded amount
is 15.94%, which was found by Lewkowitsch in a sample having an
acid value of 146.5 and a saponification value of 153. Ulzer gives
4.76 and 5.9% as the quantity of unsaponifiable matter in two samples
of Austrian rosin.

Acetyl Value.—K. Dieterich has obtained the following results
for this value:

> By titration of the acetylated resin with alkali.........155.8
> By back titration, after saponification (ester-
>   number) ....92.1 to 95.4
> Difference (= saponification number of acetylated
>   resin) ....251.2 to 274

Kitt has found the *carboxyl value* of colophony to be insignificant
(about 0.5%).

Gregor and Bamberger obtained negative results for the *methoxyl
value* of colophony.

The *iodine number* of colophony has been estimated by various
observers with curiously variable results (page 12). The esti-
mation has a practical value for the detection of colophony in
shellac, but the recorded figures should be verified by examining a
typical sample of colophony side by side with the shellac in
question.

Detection and Estimation of Colophony.—When unmixed with
interfering substances colophony is readily recognised by its physical
and sensible characters (page 90).

A valuable reaction for colophony, originally suggested by Lieber-
mann, but modified by Storch and Morawski, consists in treating the
substance with acetic anhydride, cooling the liquid, and separating
the acetic anhydride with a pipette or other suitable arrangement.
Sulphuric acid of 1.53 sp. gr. is then allowed to flow gently into the
tube containing the acetic anhydride, when a reddish-violet colour
will be immediately produced at the junction of the two liquids if
colophony be present. The colour soon changes to reddish-brown.
According to Allen, a preferable plan is to place from 10 to 20
drops of the acetic anhydride solution in a flat porcelain dish
(or the inverted cover of a porcelain crucible), and cautiously add a
drop or two of sulphuric acid of the above strength. The colouration
is seen more readily against a white background than when a test-tube
is used.

Fatty acids do not produce a similar colour, but cholesterol and
some other substances simulate the reaction of colophony.[1] Cholesterol
may be separated by shaking the substance with aqueous soda and
ether, separating the alkaline liquid, and acidifying it with sulphuric
acid. The precipitate of resin acids should be separated and dis-
solved in acetic anhydride.

P. Foerster (Ann. Chem. Anal. Appl., 1909, 14, (14) has sug-
gested the following modification of Halphen's test for the detection
of rosin oil in mineral oils, which enables traces of colophony to be
detected in other substances. Two solutions are necessary: a. 1
part by volume of phenol in 2 parts of carbon tetrachloride. b. A
solution of 1 part of bromine in 2 parts of carbon tetrachloride.
When a small amount of colophony is dissolved in 2 c.c. of solution
a, and the basin is brought close to solution b, the bromine vapours
given off by the latter produce at the point of contact a blue colouration,
which changes to violet under the continued action of the bromine.
When rosin oil is present a violet colour is produced at once. It is
usually necessary before applying the test to isolate the colophony.

Other qualitative tests for resin acids and approximate methods of
separating them from fixed oils, etc., are described in Vol. 2.

A fair approximate estimation of rosin when in admixture with
neutral fatty oils may be effected by dissolving the sample in a mixture
of alcohol and ether, and titrating with standard sodium hydroxide
solution. Taking 165 as the average acid number of colophony, each
c.c. of N/10 alkali neutralised by the sample represents 0.0340 grm.
of colophony present. As the neutralising power of rosin varies
materially, the result obtained as above can only claim approximate
accuracy. It is, of course, further affected by free fatty acids, which,
if present in quantity, will entirely vitiate the estimation. The
process is, however, convenient and of considerable practical utility.
Thus, the author has employed it for approximately ascertaining the
proportion of rosin in a mixture of that substance with linseed oil used
as bird-lime.

For the estimation of colophony in cerasin and paraffin, the sample
should be boiled several times with 70% alcohol. The alcoholic
liquid is filtered when quite cold, and the filtrate distilled. The resi-
due of resin is dried at 110° to 115° and weighed. If fatty acids are

[1] This test is also used to detect palm oil as colouring matter in oleomargarin, etc. (Cramp-
ton's method), see Vol. 2, p. 310.

present, they will be extracted with the resin and must be subsequently separated.

The separation of fatty and resin acyls is necessary for the estimation of colophony in soap. It presents considerable difficulties, as the fatty acids vary somewhat in chemical and physical characters according to their source, and colophony is itself of complex and variable composition. The processes practically available are those of Barfoed, Gladding, and Twitchell, or modifications or combinations of these. These methods are fully described in Vol. 2. Twitchell's is by far the most satisfactory process, and is sufficiently accurate for many purposes. When, however, it is desired to estimate the proportion of colophony in soap with the greatest attainable accuracy, a combination of Twitchell's and Gladding's methods, described by Holde and Marcusson (*Mittheil. Königl. tech Versuchsanstalt.*, 1902, 40), may be advantageously employed. In this process special attention is paid to the washing of the immiscible solvents employed, the resin acids soluble in water are recovered, and the unsaponifiable matter natural to the colophony is estimated or allowed for. The process is as follows:

A quantity of the sample representing about 5 grm. of fatty and resin acids is boiled with 50 c.c. of alcoholic potassium hydroxide for half an hour under a reflux condenser. The alcoholic solution is then evaporated, the residue dissolved in water, and any unsaponifiable matter removed by agitation with ether. The aqueous layer is separated and acidified with hydrochloric acid. Soaps containing no unsaponified fat or unsaponifiable matter may be directly dissolved in water and decomposed with acid. The separated acids are removed by shaking with ether; the aqueous acid solution is neutralised, evaporated to about 25 c.c., reacidified, and shaken out with ether. After distilling off the ether from the united ethereal extracts, the residue of resin and fatty acids is dissolved in 50 c.c. of absolute alcohol, and the fatty acids converted into esters by passing a moderately rapid current of dry hydrogen chloride gas through the solution cooled by ice-water to a temperature not above 10°. When the operation is complete (which is usually the case in from 1 to 2 hours), the liquid is allowed to stand for half an hour at the ordinary temperature. It is then diluted with five times its volume of water, and boiled under a reflux condenser for half an hour. The cooled solution is agitated with several successive quantities of ether until the extracts are colourless. The

aqueous liquid is neutralised, evaporated to 50 c.c., acidified, and repeatedly extracted with small quantities of ether to recover the water-soluble constituents of colophony. The mixed ethereal solutions are shaken out with about 50 c.c. of a solution containing 10 grm. of potassium hydroxide, 10 grm. of alcohol, and 100 c.c. of water, when a brown layer usually separates out between the ether and the alkaline solution, and is drawn off with the latter. This layer contains a considerable portion of the resin soap, which is only slightly soluble in the potash solution. The ether is shaken with water to remove soluble resin soaps; then with 2 successive quantities (10 c.c.) of the potash solution; and finally with water until the washings are colourless.[1] The alkaline liquid is now acidified and agitated with ether until completely extracted. The acid solution is neutralised, evaporated in a small bulk, reacidified, and again shaken out with ether. The total ether extracts are washed with 20 c.c. of water, and the ether distilled off. The residue of resin acids so obtained—still contaminated with unchanged fatty acids—is treated with several small successive additions of absolute alcohol to remove the last traces of water, and weighed. The fatty acids still remaining in the resin acids are removed by Gladding's process. From 0.4 to 0.6 grm. of the resin acids, obtained as above, should be placed in a 100 c.c. stoppered and graduated cylinder and dissolved in 20 c.c. of 95% alcohol.[2] A drop of phenolphthaleïn solution is added to the alcoholic solution, and then concentrated sodium hydroxide solution (1 of NaOH to 2 of water) until the reaction is just alkaline. The loosely-stoppered cylinder and its contents are heated for a short time in the water-bath, then cooled, and ether added up to the 100 c.c. mark. 1 grm. of dry powdered silver nitrate is added, and the contents of the cylinder are shaken for 15 minutes to convert the fatty and resin acids into silver salts.

When the insoluble salts have completely settled (preferably after standing overnight), 70 c.c. of the solution should be pipetted into a second 100 c.c. cylinder and shaken with 20 c.c. of dilute hydrochloric acid (1:2). The ethereal layer is drawn off, and the aqueous liquid twice shaken with ether. The united ether extracts are washed

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[1] In the presence of fish-oil acids or much colophony the washing with water must be very thorough.
[2] If only a small amount of resin acid is obtained, the prescribed proportions of the ether-alcohol mixture must be correspondingly altered, while in the case of a large yield of acids, it is advisable to dissolve the whole in so much 95% alcohol that 20 c.c. of the solution shall contain 0.5 grm. of resin acids.

with water, filtered, and the ether distilled off. The residue, amounting to about 10 c.c., is evaporated, dried for a short time at 110° to 115°, and weighed. The weight of the resin acids so found is calculated back into the first weight (impure acids) obtained, and then on the original substance taken. The percentage found is corrected by the subtraction of 0.4%, this allowance being made for a small amount of unesterified fatty acid which is always present. ᵣAs colophony contains an average of 8% of unsaponifiable matter, a second correction is necessary, the true percentage of colophony of the substance under examination being found by the following equation, in which the corrections are combined:

$$100 \; \frac{(\text{Percentage of resin acids found} - 0.4)}{92} = \% \text{ of colophony}$$

COLOPHONATES. RESINATES.

Colophony dissolves in solutions of alkali hydroxides, and of alkali metal carbonates, with formation of so-called resin soaps consisting of impure abietates.

Commercial Varieties.—The lead, manganese, calcium, zinc, potassium, and sodium salts are now articles of commerce. Potassium and sodium resinates have marked detergent properties, and are extensively employed in the manufacture of the commoner kinds of soap. Resin soaps have a remarkable emulsifying power (see H. Collier, *Phar. J.*, 1889 [3], **20,** 751), and this property finds an extensive application in the manufacture of sheep dips, kerosene emulsions for spraying, etc., and phenolic disinfecting fluids. Creolin, lysol, Little's sheep dip, and Jeyes' fluid are examples of such preparations (see Vol. 3). The metallic resinates of manganese and lead are often added to boiled linseed oil, and are now employed in the manufacture of varnishes. Colophonium has always been used in the varnish industry, but formerly it was only employed for special purposes. This soft gum could only be combined with a small quantity of oil, and the resulting varnish rubbed up as a white powder. Zimmermann first observed that greater hardness could be obtained by the neutralisation, or partial neutralisation, of the resin acid by the addition of an oxide of the alkaline earths. This method has been further investigated, and at the present time large quantities of these salts are used commercially.

Resins esters are now produced from colophony by condensation

with higher and lower alcohols and phenols. These compounds are of some importance because they are found in commerce under fancy names, as gum or shellac substitutes, or sold as ester gum.

Identification and Valuation.

1. **Resin soaps.**—Sodium resinate is a deliquescent brown powder which is very soluble in water. The taste is resinous and very acrid. Resin soaps differ from those of the fatty acids in not being readily precipitated from their aqueous solutions by the addition of brine. Resin soaps are also differentiated by their solubility in ether or ether-alcohol, a fact utilised by Barfoed for the separation of fatty from resin acids. Jean and Remont have proposed to utilise the solubility of barium colophonate in alcohol to effect the same separation, while Gladding has described a method of separating fatty from resin acids based on the ready solubility of silver colophonate in ether, and almost complete insolubility of silver oleate, etc., in the same menstruum, even in presence of some alcohol.

2. **Driers (Lead and Manganese Resinates).**—These preparations of colophony, commercially known as resinate driers, are of very variable composition. They are either prepared by melting rosin with the oxide of the metals or by the addition of a soluble metallic salt to the aqueous solution of a resin soap. The commercial products are mostly prepared by the former method, consequently they usually contain a large proportion of free resin acid. The fused resinates are brown to dark brown in colour with the appearance of dark rosin. Commercial precipitated lead resinate is light brown, and the corresponding manganese salt has a pinkish hue. Both manganese and lead resinates are used, but for general purposes a mixed resinate containing lead and manganese in the proportion of 5 to 1 is the most suitable. This product contains 8 to 9% of soluble lead and 1.5 to 2% of soluble manganese.

Meister (*Farbenztg.*, 1907, **51**, 1614) has examined a number of commercial lead and manganese resinates, and obtained the following results:

Material	Manganese, %	Manganese resinate, %	Lead, %	Lead resinate, %
Fused manganese resinate	2.5-3	45-55	....	....
Fused lead manganese resinate..	1.5	27	9-10	40
Precipitated manganese resinate.	5.7-6.5	80	....	....
Precipitated lead resinate........	....	....	20-23	80

These resinate driers are now widely used. The general physical
properties, that is, colour, hardness, etc., are of very slight impor-
tance for their valuation. The total quantity of mineral matter
present must not be taken as an approximate measure of value as
suggested by Amsel (*Zeit. angew. Chem.*, 1896, **9**, 429).

The drier must be completely soluble in linseed oil at 120°. Any
oxide which remains suspended is not only valueless as a drier, because
it cannot act at the low temperature at which the oil is treated, but it
forms a foot or turbidity which directly impairs the quality of the oil.
Although the proportion of insoluble oxide should be as small as possi-
ble, the proportion of uncombined acids should also be small, since
the presence of these acids decreases the percentage of active metal.
Although values obtained by analysis are helpful in judging the quality
of a drier, there are other important considerations. Driers of the
same apparent chemical composition behave so differently when
applied to their special use, that practical tests are extremely important.
Numbers of experiments have proved that one and the same resinate
from different sources, *e. g.*, precipitated manganese resinate, gives
varying results. Some cause oil to fatten, that is to become thick,
others bleach the oil; some give foots, others give minimal quantities
of the same. In view of these difficulties Andes has suggested the
adoption of the following methods for obtaining true information
regarding the value of the drier under examination.

For these tests it is necessary to have well-matured linseed oil which
when heated to 270° to 300° shows no signs of yielding a deposit. If this
is not available, ordinary commercial linseed oil should be first heated
to this temperature, and then allowed to stand several days before use.
The test can be made in two ways: *a.* By solution of the drier in linseed
oil, with and without heat. *b.* By solution in turpentine and mixing
the solution so obtained with linseed oil.

a. Precipitated resinates dissolve in linseed oil at ordinary tempera-
tures. The oil is shaken occasionally with 1.5% of the drier for 24
hours and then allowed to stand. Fused resinates are not soluble in
the cold, so they must be heated with the oil to a temperature of 120°.

b. Dissolve in turpentine in the proportion of 1 part to 4 parts of
turps with application of heat. Add from 5 to 10% of this solution to
linseed oil, shake together, and allow to stand.

The solutions obtained in this way are filtered into tall square bottles
and allowed to stand at least 4 days. The colour, transparency,

and the amount of precipitate is then observed. That drier is the most satisfactory which colours least, remains clear, does not thicken, and gives the smallest amount of precipitate. The drying test is also of great importance. The oil should be spread on a glass plate about 5 × 5 in. square and stood on a rack at a angle of 75° to 80°. Under these conditions the oil should dry off to an elastic skin in 5 or 6 hours.

Analysis of Driers.[1]—The resinates contain soluble and insoluble oxides of the metals. The total quantity of metallic oxide present can be found by an estimation of the constituents in the ash, while the soluble oxides can be separated from the resinate by treatment with a solvent in which the metallic resinates are soluble. R. Hefelmann (*Chem. Rev. Fett-Harz-Ind.*, 1901, **8,** 191) uses the following method: 10 to 15 grm. of the powdered resinate drier is agitated with chloroform, and filtered into a measuring flask and made up to 250 c.c. 50 c.c. of the extract are then treated in an Erlenmeyer flask with alcoholic hydrogen sulphide. The lead sulphide is well washed, dried, and weighed. The filtrate, if it contains manganese, is evaporated, and the manganese is estimated in the residue.

Estimation of Free Resin Acid.—Marcusson and G. Winterfeld (*Chem. Rev. Fett-Harz-Ind.*, 1909, **16,** 104); see also Holde (*Mineralöle und Fette*, 1905, 377). The estimation is carried out in the following way: 10 to 20 grm. of the sample are dissolved in 50 c.c. benzene. The solution is filtered, 30 c.c. of hot water coloured with methyl orange are then added, and the whole is titrated with N/2 hydrochloric acid until after warming and shaking the water layer retains a pink colour. The

[1] Max Weger (*Chem. Rev. Fett-Harz-Ind.*, 1897, **4,** 303) has written as follows respecting the valuation of resinate driers. The most active, and *a priori* the most useful drier is that in which the highest possible amount of soluble lead or manganese, respectively, are present, combined with the absence of insoluble oxides. In practice this is not the case. It is often necessary to accept a percentage of free resin acids which offer an important advantage in the processes used by the oil and varnish manufacturer. It is often desired, or for some purposes it is absolutely necessary, that the resinate should be dissolved at a low temperature, and the presence of the free resin has an important influence on the temperature at which the drier is taken up. A melted resinate containing 5% of soluble manganese would theoretically be superior to a similar resinate containing only 4%. Under certain conditions this might be the case; on the other hand, a resinate containing 4% of soluble manganese might be applicable, yet a resinate containing only 3% would suit the conditions much better. A drier suitable for the preparation of a liquid terebine might be totally unsuitable for direct use in varnishes, and *vice versa*. The special application for which the drier is intended is the important consideration. That product is not the most suitable which contains the theoretical quantity of lead or manganese, respectively, but that article which suits the total requirements of the manufacturer, relating to drying power, colour, temperature of solution, behaviour toward pigments, etc. It would be absolute foolishness, and show a total ignorance of practical conditions, to give an opinion on a drier based on analytical results, without due consideration of the special purpose for which the drier is intended. Under such conditions it would be easily possible to describe the most suitable product as unsatisfactory and *vice versa*. Even when the exact practical requirements are known, long practical experience is essential, to enable a chemist with some surety to base his opinion on an analysis of these products, and even then it would be advisable to confirm the conclusions by practical tests. Practical tests for the valuation of these products, as with most other materials used in the varnish industry, were and remain absolutely the determining factors.

benzene layer is then separated from the water, well washed, mixed
with neutral alcohol, and again titrated with a $N/10$ sodium hydroxide
solution in the presence of phenolphtnaleïn. From these two titra-
tions the amount of free resin acid present can be calculated.

3. **Hardened Rosin.**—*a. Metallic Resinates.* These substances are
now largely used as constituents of varnishes. They do not soften at
such a low temperature as ordinary rosin, and feel less sticky when
held in the warm hand. Unlike colophony they are insoluble in al-
cohol, but dissolve in linseed oil and turpentine, giving more or less
quick-drying varnishes. Water decomposes all these compounds,
e. g., the barium, calcium, strontium, and zinc salts; consequently,
although such varnishes are comparatively suitable for in-door work,
when exposed they are rapidly disintegrated. Varnishes prepared
in this manner when mixed with lead or zinc colours do not cause them
to thicken, whereas ordinary colophony, particularly with lead, sets
hard under these conditions.

b. Esters of Colophony. These compounds are pale in colour
easily soluble in oil and turpentine, and possess great brilliancy. In
alkaline solutions they are insoluble. It is stated that varnishes pre-
pared from these products dry hard and stand exposure, but, although
these statements are made, cheaper and more satisfactory varnishes
can be prepared from the commoner varieties of copal.

DRY DISTILLATION OF COLOPHONY.

When rosin is subjected to dry distillation, it undergoes decompo-
sition in a very complex manner.[1] Besides a variable proportion of
unaltered resin, it yields a large number of hydrocarbons, traces of
phenolic compounds, and various acids and aldehydes of the fatty
series. Among the last-named have been recognised acetic, propionic,[2]
isobutyric, isovaleric, caproic, heptoic, nonoic, and heudecatoic acids;
and isobutyric and valeric aldehydes.

[1] According to Bischoff and Nastvogel (*Ber.*,1890, **23,** 1919, *J.Soc.Chem.Ind.*, 1890, **9,** 927),
if rosin be distilled in a vacuum the products are fewer and more readily separated than when
the distillation is conducted at the ordinary atmospheric pressure. Working on laboratory
quantities, by repeated fractionation under 30 mm. pressure, two main fractions were
obtained. The larger of these boiled at that pressure between 248° and 250°, and after a
short time solidified to a colourless, brittle, microcrystalline mass, which was insoluble
in water, but soluble in alcohol and ether. It had the composition $C_{40}H_{58}O_3$, and was
apparently *abietic anhydride* ("isosylvic anhydride"). It had a specific rotation of $+63°$,
dissolved in a warm solution of potassium hydroxide, and on acidifying the liquid with
acetic acid gave an acid having the composition $C_{20}H_{30}O_2$, and melting at 60.5° to 62.5°.
Hence it was an isomer of abietic or sylvic acid. The other main fraction boiling at 318° to
320° contained $C_{20}H_{32}$, and was a diterpene probably identical with Deville's *colophene.*
[2] Propionic acid was observed by Renard in considerable quantity in the products of the
distillation of rosin at a red heat.

The distillation of rosin is practised commmercially on an extensive scale for the production of rosin spirit and rosin oil. The process is conducted in vertical cast-iron stills with hemispherical ends. The heat is applied directly, and distillation without steam is usually preferred, as in that case the production of spirit is less. Gas and aqueous liquid are first given off, followed or accompanied by a light, oily liquid, which boils between 80° and 250°, and constitutes the product known as *rosin spirit* (see below). At about 300°, or somewhat above, *rosin oil* commences to distil, and continues to pass over until the still attains a dull red heat. Water, containing a little acetic acid, continues to pass over throughout the process, and gases are evolved in considerable quantity.[1] The residue in the still consists of pitch or coke, according to the stage to which the distillation is pushed. The yield of rosin oil is generally about 85%, the remaining 15% including from 2.5 to 5% of rosin spirit, a small proportion of water, containing about 1% of acetic acid (*J. Soc. Chem. Ind.*, 1890, **9**, 16), pitch or coke, gases, etc.[2]

Rosin Spirit.

Rosin spirit is the lighter and more volatile oily portion of the product of the dry distillation of rosin. It is separated from the acetous aqueous liquid which distils with it, purified by agitation with sulphuric acid and sodium hydroxide (and sometimes common salt), and is then redistilled.

When thus refined, rosin spirit is a colourless liquid, insoluble in water or alcohol, but miscible in all proportions with ether, petroleum spirit, and oil of turpentine. Rosin spirit presents a close general resemblance to oil of turpentine, the odour, however, is peculiar, and the sp. gr. is more variable, ranging from 0.856 to 0.883. The behaviour of rosin spirit on fractional distillation is also different from that of turpentine oil, and other distinctions exist (see Turpentine Oil).

Rosin spirit has a peculiar and highly complex composition. According to A. Renard (*Ann. Chim. Phys.*, 1884, [6], **1**, 223), the hydrocarbons of rosin spirit include pentane, pentene, and their homologues; toluene and its homologues; tetra- and hexa-hydrotoluene, and their homo-

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[1] The gases contain carbon monoxide, ethylene, butylene, and pentine, and are said to be powerfully anæsthetic.
[2] E. J. Mills has recorded the densities and bromine-absorptions of the products distilling at frequent intervals during an entire operation. The sp. gr. increased from 0.909 to 1.0030 at the end of 20 hours, and then fell to 0.970. The bromine-absorption of the first product was 142% and gradually fell to 32% (*J. Soc. Chem. Ind.*, 1885, **4**, 328).

logues; terpenes, etc.[1] Deville found colophene (boiling between 318°
and 328°) in the last fractions of rosin spirit.

About one-half of rosin spirit consists of hydrocarbons boiling below
120°.

One of the most characteristic constituents of the lighter fractions
of rosin spirit is the hydrocarbon *heptine*, C_7H_{12}, which appears to
have the constitution of a *methyl-propyl-allene*. It boils at 103° to
104°, and has a sp. gr. of o. 8031 at 20°. Heptine is colourless, mobile,
of characteristic odour, and is soluble in alcohol and ether. It absorbs
oxygen very readily, and is without action on an ammoniacal solution
of cuprous chloride or silver nitrate. By treatment with concentrated
sulphuric acid it is polymerised, with formation of a *di-heptine* $C_{14}H_{24}$,
boiling at 235–250°, and rapidly oxidising and resinifying in the air.
By the action of water and air it is converted into a crystalline *hep-
tine glycol*, $C_7H_{12}(OH)_2,H_2O$, soluble in water, alcohol, and ether.
The crystals, as also the original hydrocarbon, when warmed with an
acid (*e. g.*, hydrochloric, sulphuric, tartaric), give a series of coloura-
tions, the mixture passing through shades of yellow, red, green, and
deep blue; and on adding this liquid to alcohol a magnificent green
colour is communicated to it (G. H. Morris, *Trans.*, 1882, **41,** 172).
Rosin spirit itself does not give the reaction distinctly, and Allen had
not succeeded in applying it to the detection of rosin spirit in turpen-
tine oil.

Rosin Oil.

Rosin oil, or *resin oil*, is the heavier and less volatile portion of the
product resulting from the dry distillation of colophony. The crude
oil first obtained can be purified by washing with a small percentage
of sulphuric acid, followed by treatment with lime-water and redis-
tillation, with or without the aid of steam. A superior product is
obtainable by redistilling the oil over solid sodium hydroxide, with the
aid of a current of superheated steam. Lime-dust and other acid-
removing agents have also been employed, and a very fine oil is said
to be obtainable by mixing the crude oil with cottonseed oil prior to
distillation.

Commercial Varieties.—Commercial rosin oil is a viscid liquid

[1] For a complete list of the constituents of rosin spirit, with their formulæ and b. p.,
see E. M. Holmes, *Pharm. Jour.*, 1899, **1,** 99.
    G. H. Morris has published a valuable list of researches on rosin spirit prior to 1882
(*Trans.*, 1882, **41,** 172).

varying in colour from water-white to dark brown, and is sometimes opalescent from the presence of water. It generally exhibits a strong bluish or violet fluorescence, which is apparent even in its dilute ethereal solutions. The bloom is less marked in refined rosin oil, and can be destroyed more or less completely by exposure to air and sunlight, by treatment with hydrogen peroxide, by addition of nitrobenzene, nitro- or dinitro-toluene, dinitro-naphthalene, etc., or by heating with sulphur.

Chemical Composition.—The chemical composition of rosin oil is not perfectly understood. It often contains a notable proportion of *abietic acid*, or possibly abietic anhydride, but the greater part consists of a mixture of hydrocarbons of high b. p.[1]

The following results of analyses of samples of rosin oil examined in Allen's laboratory in 1886 show the variation in the character of the commercial article. The sp. gr. was determined by the bottle, the oils being too viscous to allow a plummet being satisfactorily used. The hydrocarbons were isolated as described on page 30, and the resin acids subsequently recovered by acidifying the alkaline liquid.

Description of sample	Sp. gr.	Resin acids	Hydrocarbons	Bromine absorption, dry		Bromine absorption, wet	
				Total	AsHBr.	Total	AsHBr.
Very pale refined oil..	0.990	....	96.9	110.0	11.8	....	......
Pale oil, special......	0.982	6.4	93.9	105.1	4.8	....	......
Pale sweet oil.......	0.979	1.1	....	63.0	4.7	56.5	13.6
Ordinary oil.........	0.985	17.8	81.2	138.5	9.7	....	......
Common dark oil (not the commonest....	1.099	11.1	88.6	66.6	.7.6	....	......
Crude oil..........	0.990	....	....	60.8	3.9	47.0	11.2
Pine oil...	0.986	....	....	73.9	5.1	51.9	8.9
Ink oil....	1.006	....	....	....	....	....	......

It will be observed that the bromine absorptions, as determined by the dry process (Vol. **2**) are extremely variable. There is also a wide

[1] According to A. Renard (*Compt. rend.*, 1887, **105**, 865; **106**, 856, 1086), about 80% of the hydrocarbon constituents of rosin oil consists of *diterebentyl*, $H_{16}C_{10}$—$C_{10}H_{16}$. This body forms a colourless oil which has a sp. gr. of 0.9688 at 18°, and boils at 343° to 346°. Its specific rotation is +59°. If a thin layer of diterebentyl is exposed to the air for some time, it absorbs about 10% of oxygen and forms a sticky varnish. When treated in the cold with strong sulphuric acid, diterebentyl yields a monosulphonic acid as a brownish-black mass soluble in water, alcohol, and ether. Its solution is fluorescent, appearing brown by transmitted and green by reflected light.

If the fraction of rosin oil boiling between 300° and 360° be treated with sulphuric acid, the diterebentyl becomes polymerised or converted into the sulphonic acid mentioned above. If the oily portion be separated and distilled, the distillate contains *diterebentylene*, $C_{20}H_{28}$, and *didecene*, $C_{20}H_{36}$, which together form about 20% of the hydrocarbons of rosin oil (A. Renard, *Compt. rend.*, **106**, 1086).

divergence between the results by the dry and those by the wet process, and the absorptions of different samples are not even comparative. The figures obtained by the wet process are less than those yielded by the dry, while the reverse is the case with shale and petroleum products. The results were confirmed by repetition, and hence the anomalous figures are not errors of experiment.

A recent analysis (1903) of a commercial sample of rosin oil made by J. Thompson, in Allen's laboratory, gave the following results:

	%	Combining weight
Resin acids, weighed......................	15.72	289
Resin acids, titrated (as $C_{20}H_{30}O_2$)........	16.91 } 98.62	302
Unsaponifiable matter.................	81.71 }	

Uses.—Rosin oil has a large legitimate employment as a lubricant, especially for machinery and wagon-wheels. It is used in the condition of rosin-grease, and in admixture with olive, rape, and other oils.[1] Mixed with rape oil, it has been employed for adulterating olive oil, and it is frequently added to the inferior kinds of boiled linseed oil. Castor oil has been systematically adulterated with rosin oil. Rosin oil is sometimes added to the denser kinds of mineral lubricating oil, which are then treated with lime to make axle grease. It is also much used in making printers' inks mixed in varying proportions with linseed oil.

Adulterants.—This oil is sometimes adulterated with mineral oil, but it is more often the case that it is used to adulterate the more expensive oils, and mineral lubricating oils.

General Properties.—Rosin oil varies in colour from dark brown to water-white, according to the degree of refining to which it has been subjected. The refined product has but little odour at ordinary temperatures, but when strongly heated it gives fumes neutral or nearly neutral in reaction to wet litmus-paper, having a marked odour of resin, which burn readily with a smoky flame. When rosin oil is heated no distillate is usually obtained below 300°.[2] The taste is pecu-

[1] Information respecting the mode of manufacture of rosin oil, and the composition of various lubricants containing it, will be found in the *J. Chem. Soc.*, 1873, **26**, 304, 305, and 1175, and also *J. Soc. Chem. Ind.*, 1902, 1336. The practical uses of rosin and rosin oil are also described in the *J. Soc. Chem. Ind.*, 1904, **23**, 328.

[2] However often rosin oil be distilled, the product always contains a small quantity of terpenoid bodies, which are probably produced by depolymerisation of the heavier hydrocarbons by a process of "cracking," similar to that undergone by the hydrocarbons of petroleum under the same conditions.

liar, and the after-taste is strong, nauseous, and highly characteristic. When treated with strong sulphuric acid as in Maumené's test for fixed oils, rosin oil usually gives a rise of 18° to 20° in temperature when 50 grm. are treated with 10 c.c. sulphuric acid (sp. gr. 1.84), (see Vol. 2, p. 58), and forms a reddish-brown liquid which separates into 2 strata. Nitric acid is sometimes without immediate action on rosin oil, but if the mixture be warmed, a violent reaction often ensues suddenly, and after cooling the oil is found to be converted into a more or less brittle red resin. When agitated with one-third of their volume of fuming hydrochloric acid, most samples of rosin oil gradually acquire a dark and ultimately black colour. Chlorine and bromine act somewhat violently on rosin oil. The proportion of bromine absorbed is very variable.

Specific Gravity.—Crude rosin oil has a sp. gr. ranging from 0.96 to 1.1, but when refined the figures are much more constant, and vary only from 0.97 to 0.99.

Solubility.—Rosin oil is insoluble in water, and only slightly soluble in alcohol. It is miscible in all proportions with fatty oils, mineral oils, ether, chloroform, carbon disulphide, turpentine oil and petroleum spirit. The greater solubility of rosin oil in glacial acetic acid compared with that of mineral oil has been suggested by Valenta and Feigerle as a means of its detection in mixtures. Demski and Morawski used acetone for the same purpose. These methods do do not always give very satisfactory results.

Optical Properties.—Rosin oil is strongly dextrorotatory, and this value varies from +30 to +50 for the sodium ray. To render highly coloured rosin oil fit for optical examination, Valenta treats it with potassium ferrocyanide and then filters.

Identification.—Renard has observed that anhydrous stannic chloride develops a violet colouration with rosin oil. Allen found it more convenient to employ stannic bromide than stannic chloride, and that the test is much more delicate and under control if free bromine be also present and the oil and reagent be previously dissolved in carbon disulphide. The stannic bromide is prepared by allowing bromine to fall drop by drop on granulated tin contained in a dry flask immersed in cold water. The addition is continued until the permanent colouration of the product shows that the bromine is in excess. A further moderate addition of bromine is then made, and the liquid is then diluted with three or four times its volume of carbon disulphide,

in which the stannic bromide is readily soluble. To employ the reagent,
which when thus prepared appears to be perfectly stable, a few drops
of the sample should be placed in a dry test-tube and dissolved in
about 1 c.c. of carbon disulphide. The bromide reagent is then gradu -
ally added, when if rosin oil be present the liquid will rapidly acquire a
fine violet colouration, which in the case of pure rosin is so intense as to
necessitate dilution with carbon disulphide before the colour is percep-
tible.   On standing for some time, a deposit of violet colour is formed
at the bottom of the tube, and if the remaining liquid be poured off and
the residue be warmed with a little carbon disulphide, a violet or purple
solution of great purity of tint may be obtained.   This mode of operat-
ing is especially useful in the presence of foreign oils or impurities
which disguise the colour due to rosin oil.   In the presence of much
mineral oil Allen found it a good plan to first mix the sample with a
solution of stannic bromide in carbon disulphide, and then add, drop
by drop, a solution of bromine in carbon disulphide, by which means
the violet colouration may often be obtained unobscured by any colour
produced by the mineral oil.

The violet substance to which the colouration is due appears to be
permanent in the air, but the colour is destroyed by addition of alcohol,
ether, ammonia, or water.

Chloroform may be substituted for carbon disulphide in the fore-
going test.

Instead of dissolving the oil in carbon disulphide it may be dissolved
in glacial acetic acid, and the greater solubility of rosin oil than mineral
oils in this menstruum affords a means of applying the test to mixtures
of the two in a very advantageous manner.   Thus, if the sample to be
tested be shaken in the cold with twice its volume of glacial acetic
acid, and the acid layer separated and tested with a solution of stannic
bromide and bromine in carbon disulphide or chloroform, a fine violet
colouration will be produced if rosin oil be present.   The colouration
produced in acetic acid solution appears to be of decidedly bluer shade
than that obtained when carbon disulphide is used as the solvent for
the oil, but the tint in the latter case varies considerably with the pro-
portion of the reagent used, a large excess having a tendency to produce
reddish tints.

A test for rosin oil in the presence of mineral and saponifiable oils
has been based on Storch's reaction with sulphuric acid, but in its
original form the test is fallacious in presence of cholesterol, etc.   As

modified by T. Morawski, the sample is dissolved in acetic anhydride, with the aid of gentle heat, the liquid cooled, and a few drops of sulphuric acid of 1.53 sp. gr. allowed to flow down the side of the test-tube, so as not to mix with the contents. In presence of rosin oil or rosin, a violet-red colouration will be produced at the point of contact. Holde modifies the test by simply shaking up the oil with sulphuric acid of 1.53 sp. gr. In a subsequent paper he increases the strength of the acid to 1.624 sp. gr. which is stated to give the reaction more promptly. The different modifications of the test have been investigated by A. Grittner (*Zeits. angew. Chem.*, 1891, **4**, 265), who considers the weaker acid preferable, since with the stronger, other oils are liable to give colourations which more or less obscure that due to rosin oil. For train oils containing but a small proportion of rosin oils, Morawski's method is preferable, but with dark oils Holde's is the better. Morawski's test is inapplicable to dark lubricating mineral oils. In the possible presence of resins, such as colophony or shellac, it is necessary to saponify the oil and test the unsaponifiable matter. A modification suggested by Holde (*Mitt. Königh. Vers.-Anst., Berlin*, **6**, 88) is to agitate the oil to be tested with alcohol, and apply the test to the separated alcoholic liquid or the residue left on its evaporation. By careful procedure, very small proportions (*e. g.*, 1%) of rosin oil can be detected by the above test.

From experiments made in Allen's laboratory, J. Thompson considered the following method of operating to be the most satisfactory: About 1 c.c. of the oil to be examined is placed on a porcelain crucible lid and 2 c.c. of acetic anhydride well mixed with the oil and warmed. In the case of oils not completely soluble in acetic anhydride, the mixture should be made in a test-tube, and the lower layer separated and placed on the porcelain lid. A drop or two of sulphuric acid (sp. gr. 1.53) is then added to the acetic anhydride solution, when a beautiful purple colouration will be obtained in the presence of rosin oil, rosin, etc. When the test was performed as above described on a flat or slightly concave porcelain surface, better results were obtained than by pouring the acid down the side of the test-tube.

The colourations obtained by the stannic bromide and acetic anhydride and sulphuric acid tests for rosin oil are mainly due to the hydrocarbon oils present, as is shown by the following results obtained in Allen's laboratory:

	Resin acids †	Unsaponifiable matter
Stannic bromide............	Faint coloration on standing.	Strong purple colour.
Acetic anhydride and sulphuric acid (1.53 sp. gr).	Faint purple, fading immediately.	Brilliant purple, fading in a few minutes.

Another colour test for the detection of rosin oil in the presence of mineral oils, etc.,* has recently been described by G. Halphen (*J. Pharm. Chim.* 1903, **16,** 478), and is based on the fact that rosin oil gives an intense violet and blue colouration with a solution containing bromine and phenol, while mineral oils give only a brown colour with a slight violet fluorescence. The presence of water or alcohol interferes with the test. The substances causing the colouration are apparently identical with those giving the Liebermann reaction, and these can be extracted with strong alcohol, when the dry residue gives the colour with greater intensity. The test is carried out as follows: A drop of the oil to be examined is thoroughly mixed with 2 c.c. of a solution of crystallised phenol in carbon tetrachloride (1 in 2) in a porcelain crucible, and bromine vapour, from a flask containing bromine dissolved in carbon tetrachloride (1 in 4), allowed to fall into the crucible. The reaction is complete in from 5 to 10 seconds. Comparison tests with samples of known composition should be made, when less than 10% of rosin oil may be detected. Chinese wood oil gives a carmine colouration with violet or blue tinge, and marine animal oils give a carmine colour. Other oils give either much fainter or only indefinite reactions, among the latter being most vegetable oils.

The detection of rosin oil in fatty oils is based on its isolation by the method described in Vol. 2, pages 77 and 78, and its subsequent identification by its taste, odour on heating, sp. gr., optical activity, reaction with stannic bromide, and formation of a grease with slaked lime. Some of these tests are applicable to the original mixture of fatty and rosin oils. If the accurate estimation of the rosin oil be desired, it will often be necessary to add to the weight of the hydrocarbons or ether residue that of the resin acids, after separation from the fatty acids as described in Vol. 2, page 77.

The detection of rosin oil in admixture with the mineral lubricating oils may be affected with tolerable ease and certainty, but the positive recognition of a moderate proportion of mineral oil in such a mixture is more difficult. Any optical activity of the sample or purple reaction

with stannic bromide affords definite proof of the presence of rosin oil, and in many cases its existence is evident from the taste of the sample and its odour on heating. A high sp. gr. and bromine absorption, and a violent reaction with nitric acid, also afford strong evidence of the presence of rosin oil.

Estimation.—Valenta and Feigerle (*Dingl. Polyt. J.*, **253,** 418); and Demski and Morawski (*Dingl. Polyt. J.*, **258,** 82) have each suggested methods for the detection and estimation of rosin oil in mineral lubricating oils. J. Lewkowitsch considers the former method, which can be carried out as follows, the most reliable, although the various petroleums considerably affect the accuracy of the result: 2 c.c. of the oil should be treated with 10 c.c. of glacial acetic acid (sp. gr. 1.0562 at 15°), and heated for five minutes to 50° in a loosely-corked test-tube immersed in a water-bath. The mixture is then passed through a small filter and the middle portion of the filtrate collected. A weighed quantity of the filtrate is then titrated with standard alkali and phenolphthaleïn, whereby the weight of acetic acid present can be calculated, and the difference between the amount thus found and the weight of the portion of filtrate operated on gives the weight of oil dissolved by the acetic acid in that quantity of the filtrate.[1] When examined in this manner, the solubility of mineral lubricating oil (apparently from petroleum) varied from 2.67 to 6.50 grm. for 100 grm. of glacial acetic acid, while a sample of crude rosin oil of 1.0023 sp. gr. showed a solubility of 16.87%. The solubility of a mixed sample does not, however, increase regularly with the proportion of rosin oil present.

Detection of Adulterants.

Mineral Oil.—H. Holde (*Mitt. Kgl. techn. Versuchsanstalt*, Berlin, 1902, 39) has suggested a method which has proved successful for the detection of even small quantities of mineral oil in rosin oil. The test is carried out as follows: 10 c.c. of the oil under examination are vigorously shaken in a separating funnel with 90 c.c. of 96% alcohol (by weight). If any noticeable quantity of the oil remains undissolved, then mineral oil in considerable quantities is undoubtedly present. This conclusion can be confirmed by first allowing the undissolved

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[1] The presence of rosin acids in the rosin oil would alter its solubility, and also make the determination of the acetic acid inaccurate. It would be better to neutralise the greater part of the acetic acid, dilute with water, and extract the rosin oil by agitation with ether.

oil to settle and, after washing it with a small quantity of 96% alcohol, determining its refractive index. Mineral oils have a refractive index below 1.5330 at 15° to 20°. In doubtful cases the undissolved oil can be further treated in the following manner, and again tested in the refractometer. If only traces of oil remain undissolved by the preliminary treatment with 99% alcohol (by weight), the alcoholic solution is diluted with sufficient water to cause a very apparent milkiness in the liquid. After the solution has been allowed to stand at least 24 hours, the alcoholic solution is separated from the precipitated oil drops which should not have a greater volume than 1 c.c. The oil is then washed with a few c.c. of 96% alcohol, and the residue is again dissolved in 20 c.c. of 96% alcohol at ordinary temperature. From this solution by the addition of water a few drops of the oil are again precipitated, and after the solution has been allowed to stand these oil drops are separated, washed first with cold alcohol and then with hot alcohol in a small glass evaporating dish. When the alcohol has been evaporated and the oil cooled the refractive index of the residue is determined. If a lower figure than 1.5330 is found, then mineral oil was present.

Rosin grease is made by stirring together rosin oil and slaked lime. One method of preparation consists in stirring the rosin oil with about three-fourths of its weight of slaked lime made into a cream with water. The mixture rapidly solidifies, extruding the superfluous water, which is run off, and the grease is then diluted by gradually stirring in a further quantity of oil, until the desired consistency is attained. The oil used for diluting may be rosin oil, petroleum oil, or neutral coal-tar oil ("grease oil"). Rosin grease is also made by mixing dry slaked lime with rosin oil, without water, or by mixing the lime with mineral or coal-tar oil, and adding the rosin oil afterward. Barium sulphate, gypsum, whiting, and other make-weights are also added. Cheap greases are thus prepared, which are used to lubricate the iron axles of colliery trucks and ordinary road vehicles. Rosin grease rapidly acetifies by heat and friction, and hence is not adapted for the lubrication of brass bearings.

The formation of rosin grease has been attributed by E. J. Mills to a supposed property possessed by the unsaturated hydrocarbons contained in rosin oil of combining directly with lime and other bases ("Destructive Distillation," 4th edition, 1892, p. 97). The true explanation is that crude rosin oil invariably contains a considerable

percentage of resin acids (undecomposed colophóny), which have
distilled over with the hydrocáfbons, and it is the combination of these
acids with the lime which is the real cause of the formation of rosin
grease. According to L. Archbutt, refined rosin oil, which has been
freed from resin acids, is incapable of forming a grease with lime;
while, on the other hand, the larger the percentage of resin acids
contained in the crude rosin oil, the stiffer the grease which can be
formed.[1]

Description of rosin oil	Resin acids
A. "Pale refined,"..	0.14%
B. "Medium,".. •..................................	5.80%
C. "Hard-run,"...	21.30%

The acids extracted from each sample were quite hard and brittle.
20 grm. or each of the above oils was stirred with about 45 c.c. of a cream of lime, con-
taining about 15 grm. of slaked lime. The mixture made from sample A did not per-
ceptibly thicken on stirring and formed no solid grease on standing. Both the other
mixtures set. The hydrocarbons isolated from sample C by dissolving the oil in ether,
agitating the liquid with sodium hydroxide, and evaporating the separated ethereal layer,
showed no tendency to emulsify when treated with milk of lime, even after a long period.

Archbutt and Deeley give the following analyses of 2 samples
of rosin grease: For methods of analysis (see Vol. 3, p. 175.)

	A	B
Hydrocarbon oil....................	87.7%	86.6%
Resin............................	3.7%	7.0%
Slaked lime (CaH₂O₂)...............	6.4%	4.5%
Water, etc. (by difference)........	2.2%	1.9%
	100.0	100.0

Slaked lime (CaH_2O_2)

COPALS.

Occurrence.—The copals comprise a number of recent, recent
fossil, and fossil resins, found in nearly all tropical and subtropical
countries of the world. Africa is the home of the hardest and most
prized varieties, but medium, hard, and soft resins are also found in
that continent. There is much doubt as to the actual origin of the
various resins.

Zanzibar copal is undoubtedly furnished by the tree *Trachylobium
verrucosum;* Kauri comes from the *Dammara australis,* and the South

[1] The percentage of resin acids in 3 samples of commercial rosin oil was determined
by Archbutt by dissolving a weighed quantity of each oil in ether, shaking out with sodium,
and weighing the resin acids recovered from the hydroxide solution. The following results
were obtained:

American resins are derived from *Hymenæ courbaril*. Large quantities of copals are also obtained from Asia, and the west coast of Africa, but the actual botanical sources are not known.

Commercial Varieties.—The commercial copals may be classed into 5 groups.

a. East African copals—Zanzibar, Madagascar, Mozambique, and Lindi.

b. West African copals.

c. Manila copals.

d. Kauri copals.

e. South American copals.

Although there are many varieties of East and West African copals, it is only possible to differentiate between them in very few cases. The East African resins shipped from Zanzibar are characterised by a peculiar indented surface commercially known as the "goose skin." These resins are cleaned and graded according to colour, etc., at the place of export. The West African varieties arrive at the ports of Europe in their natural condition. Benguela copal, red Angola copal, pebble copal, and Sierra Leone copal each possess characteristics which enable the expert to identify them. At the copal washing establishments in Europe the natural resins are brushed and treated with alkaline solutions of varying strengths to remove the oxidised crust with which they are more or less coated. The cleaned product is then graded according to general appearance, size, colour, hardness, etc. By this treatment, resins from various sources with similar characteristics are batched together, and for commercial purposes are given a name which appears most suitable, irrespective of the original source. The Manila copals include all the Asiatic fossil resins at present known. Some have special characteristics, but others are so like gum Kauri that it is almost impossible to distinguish them from the latter: the slight difference in the smell affords a clue to the expert, but many varieties of this copal cannot be differentiated. They are at times forwarded to Europe in their natural state, but more often they are washed at some central station and classified according to their physical properties. South American copals are not important commercial articles. The so-called Brazilian copal of commerce has all the properties of the West African copals; very probably it is derived from this source.

Chemical Composition.—As previously stated, many of the resins are of unknown origin, and the methods adopted for obtaining these

percentage of resin acids (undecomposed colophony), which have distilled over with the hydrocarbons, and it is the combination of these acids with the lime which is the real cause of the formation of rosin grease. According to L. Archbutt, refined rosin oil, which has been freed from resin acids, is incapable of forming a grease with lime; while, on the other hand, the larger the percentage of resin acids contained in the crude rosin oil, the stiffer the grease which can be formed.[1]

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[1] The percentage of resin acids in 3 samples of commercial rosin oil was determined by Archbutt by dissolving a weighed quantity of each oil in ether, shaking out with sodium, and weighing the resin acids recovered from the hydroxide solution. The following results were obtained:

COMPOSITION OF COPALS.

	Zanzibar copal	Manila copal	(New Zealand) Kauri bush copal
Botanical origin	(Fossil and recent) *Trachylobium* and *Hymenaea* species.	*Dammara orientalis*	(Fossil) *Dammara Australis*.
Resin Acids			
A. Soluble in Am. carbonate:			
a. Crystallisable		Mancopalic, $C_8H_{12}O_2$; M.p.175°) K.1.1.[a]p= +56°; Mancopalenic. $C_8H_{14}O_2$. (100–105°) K.1.1. } 4%	Kauric or Kaurinic, $C_{10}H_{16}O_2$; (192°).K.1.1.[a]p+ 51.7; 1.5%
b. Amorphous			
B. Insoluble in Am. carbonate:			
a. Crystallisable		Mancopalic, $C_{10}H_{18}O_2$; 75 to 80%.	α-and β-kaurolic acids, $C_{12}H_{20}O_2$. (48 to 50%). Kaurinolic and Kauronolic acids. (20–22%).
b. Amorphous			
α-acid, ppted. by alcoholic lead acetate	Trachylolic, $C_{58}H_{88}O_8$, 80% (sphaero crystals, 168°).K₂ (probably).	(85–96°) K.1.1.	(α-Kaurolic (81–83°). K.1.1., Kaurinolic, $C_{17}H_{24}O_2$.(128–130°) K.1.1.
β-acid, not ppted. by alcoholic lead acetate	Isotrachylolic (106°).K₂. 4%.	(83–88°) K.1.1.	β-Kaurolic (85–87°).K.1.1., Kauronolic, $C_{22}H_{24}O_2$. (86–89°). K.1.1.
Indifferent Resins	α-copalresene(75 to 77°) (a)p(in alcohol), +12.5°; } $C_{25}H_{38}O_4$ β-copalresene } 6%. (Decomposes at 140° without melting.)	Mancopaloresene. } 12% (80–85°). $C_{22}H_{34}O$. }	Kauroresene, 12%, 63 to 65° (impure).
Essential Oil			
A. Readily volatile with steam	9%.	(B.p. 165–170°); 6%. Sp.gr. 0.810.	(150 to 160°); 12.5%. Sp. gr.0.835. Sr all.
B. Tailings	About 0.5%.	3%	0.5 to 2%
Minor Constituents Bitter principle, alkaloid, succinic acid, colouring matter, water and impurities.			
Reference			
Original	Arch. Pharm., 1896, p. 552.	Arch. Pharm., 1902, p. 202.	Arch. Pharm., 1901, p. 145.
Abst. Jour. Chem. Soc.	1897, I, 92.	1902, I, 478.	1901, I, 398.
		Another sample of Manila copal contained no acids soluble in ammonium carbonate.	

Uses.—The copals are chiefly used in the varnish and kindred industries. They are first subjécted to destructive distillation. After a certain percentage of water, gas, and oil, varying from 12 to 25%, has distilled off, the resin becomes soluble in linseed oil and turpentine. Various methods have been suggested to reduce this loss, but commercially they have not yet been adopted.

Adulteraats.—Poor-quality copals are often mixed with the harder and more prized varieties. The lowering of the m. p. may afford some information. Speaking generally, the manufacturer must at present depend largely upon his practical tests to obtain definite information regarding the quality of the resin under consideration.

General Properties.—The copals vary in colour from white through shades of yellow and red to brown and brownish-black. The same variety is often found in colours ranging from white to deep red. The natural fossil, and semi-fossil resins are mostly covered with an oxidised crust containing much mineral matter. This can be removed by treatment with alkaline solutions. When broken they generally show a conchoidal fracture and the new fracture has a lustrous appearance. Some of the resins emit characteristic odours, particularly when crushed, whereas, for example, Zanzibar copal is odourless.

a. Zanzibar Copal.—This copal has a characteristic surface covered with a number of small and large excrescences closely packed together, commercially known as the "goose skin." When the naturally opaque crust consisting of sand and atrophied resin is removed, the internal part of each piece is clear and transparent, and the colour varies from light yellow to brownish-red. Various brands of this resin are found in commerce, designated by letters. W stands for white, R represents red, while the letters A, B, C, etc., denote the size of the pieces; *e. g.*, W A means white, large. Transparent flat plates are generally the best form. They vary in size from 0.25 to 1.5 in. in width and from 0.167 to 0.5 in. in thickness. Zanzibar copal breaks with a flat fracture which is mostly brilliant in appearance, but the best varieties show a fracture half brilliant and half matt. This resin breaks between the teeth and does not agglutinate.

b. Yellow Benguela Copal.—Benguela copal is found in uneven lumps varying from 4 inches to 10 inches in diameter. These pieces are covered with protuberances, and in places have crevice-shaped indentations extending inward as far as one-third of the lump. This outward appearance is characteristic, and possessed by no other copal.

When in the raw state it is covered more or less with an oxidised crust
which is white, yellowish, or yellow in colour.   It breaks with a brilliant
fracture, is transparent, and has a light yellow to yellow, seldom a red-
dish tint.

   c. *Red Angola copal* is found in more or less round pieces, coated
with a red oxidised resin crust covering regular protuberances on the
surface of the resin.   After removal of the crust the resin is clear and
transparent.

   d. *Pebble Copal.*—This resin, as its name implies, has the appearance
of small pebbles varying in size from a pea to a pigeon's egg, and cov-
ered with a whitish coating.   The colour varies from white to yellow,
sometimes to a reddish yellow.   The resin is half transparent and
breaks with a glassy fracture.

   e. *Sierra Leone copal* is found, in pieces varying in size from a pea
to that of the fist.   They have the form of either balls or drops, and the
surface is in some cases uneven and in other cases quite smooth.   The
colour varies from colourless to a light yellow; other pieces have a
rosy-red or sea-green appearance.   It is mostly clear and transparent,
but impure pieces are milky and half transparent or opaque.   An
oxidised resin crust is rarely found on the natural resin and in any
case it is only slightly apparent.   This copal breaks with a conchoidal
fracture and emits a spicy odour, which is more noticeable when the
resin is melted.

   f. *Manila Copal.*[1]—This resin is found in large, irregular, angular
milky pieces, and is mostly covered with a white or yellowish coating.
It varies from a yellow to a honey-yellow colour, but brownish-yellow,
smoky-grey, greenish and blackish pieces are also found.   It breaks
with a conchoidal fracture, which is matt in appearance.   It is trans-
parent to semi-transparent.

   g. *Kauri Copal.*—This copal is found in rather large irregular, an-
gular or round pieces which have externally a dull appearance, and
are often coated with a whitish crust.   The colour of the resin varies
considerably, and this is often observable in one and the same piece.
It is mostly whitish, yellow, or brownish-yellow in colour, but smoky-
grey, light and deep brown pieces are also found.   The transparency

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[1] Manila Copal, C. Coffigner (*Bull. Soc. Chim.* 1907 (4) 3, 453).   Manila copal occurs in
3 varieties—hard, semi-hard, and friable.   The hard variety occurs in large pieces, vary-
ing in colour from dull white to brown.   The pieces break easily with a brilliant fracture;
some pieces are milky inside; the odour is aromatic.   The white form had the sp. gr. 1.065,
m. p. 190°, softening at 80°.   Acid value, 72.8.   Koettstorfer value, 87.   The friable
variety, which unlike the above is completely soluble in alcohol, occurs in aromatic pieces
of varying colour which break readily with a fairly brilliant fracture.   Sp. gr. 1.060,
m. p. 120°, softening at 45°.   Acid value, 145.2.   Koettstorfer value, 185.1.

varies in different parts of the same piece. Striated, smoky, and cloudy portions are to be found on nearly every lump. The Kauri resin from New Zealand is generally brown in colour, while the New Caledonian varieties are mostly yellow or white. The surface of all Kauri copals are covered with an opaque crust as thick as the finger. In the New Zealand resins this crust is mostly chalky, while the New Caledonian resins have a brown or blackish colour. When chewed this gum clings to the teeth. The taste is pleasant and the smell aromatic.

Hardness.—Generally speaking, the greater the hardness the more valuable the copal. This generalisation does not hold good for gum Kauri. This resin has been used extensively in the varnish industry, not only because of the good results obtained, but also for the ease with which it can be manipulated by the varnish manufacturers. There are other resins which melt at a lower temperature, but they have peculiar properties and are not so easy to work. Böttler has given the following scale of hardness in which Zanzibar copal is taken as the standard.

No.	Copal	No.	Copal	No.	Copal
1	Zanzibar copal.	6	Sierra Leone copal, old	11	Manila copal.
2	Mozambique copal.	7	Yellow Benguela copal	12	White Angola copal
3	Lindi copal.	8	White Benguela copal.	13	Kauri copal.
4	Red Angola copal.	9	Cameroon copal.	14	Sierra Leone (new)
5	Pebble copal.	10	Congo copal.	15	Hymenæa copal.

Specific Gravity.—The copals most frequently met with have a sp. gr. ranging between 1.03 to 1.07. This number holds good when the sp. gr. is taken directly, but when crushed and freed from air bubbles the gravity of the copals increases slightly. The difference thus observed is considerable for the softer varieties of copal and very small for the harder varieties (Böttler).

Copal	A Sp. gr. at 15° of copal freed from air	B Sp. gr. at 15° of natural copal	A—B	Position in table of hardness
Zanzibar	1.0636	1.0621	0.0015	1
Lindi	1.0695	1.0685	0.0010	3
Red Angola	1.0820	1.0680	0.0140	4
Brazilian	1.0830	1.0690	0.0140	...
Cameroon	1.0800	1.0650	0.0150	...
Kauri	1.1096	1.0480	0.0516	13[1]
Manila	1.1280	1.0690	0.0590	11[1]
Hymenæa	1.1310	1.0690	0.0620	15

[1] In Andés' scale of hardness Kauri stands before Manila

From this table it appears that Hymenæa copal, Manila copal, and Kauri copal belong to the poorer qualies; Cameroon and red Angola take up an intermediate position, and Zanzibar and Lindi copals take first place. Even from this table Brazilian copal does not appear to be a South American variety, but related to the West African copals.

Melting-point.—Böttler stated that all copals could be melted between 95° and 305°, but further experiments have proved that specimens of Lindi and Zanzibar copals do not melt below 340° and 360°. Böttler takes that temperature as the m. p. when the material begins to liquefy, whereas Bamberger takes two temperatures: *a.* When the opaque substance in a capillary tube becomes homogeneous; *b.* when the resin liquefies completely, at times with decomposition.

Copal	M. p., Böttler	M. p., Bamberger		Copal	M. p. Böttler	M. p., Bamberger	
		a	*b*			*a*	*b*
Hymenæa	95°	77°	115°	Congo copal	180°		
Cameroon	108°	96°	110°	Sierra Leone	185°		
Cameroon	108°	110°	120"	Pebble copal	220°		
Manila	112°	103°	120°	White Angola	245°	143°	340°
Manila	135°			Lindi	246°	158°	340°-360°
Kauri	126°	111°	115°-140°	Zanzibar	259°		
Yellow Benguela	170°			Zanzibar	265°		
White Benguela	175°			Red Angola	305°		

Solubility.—The usual solvents can be applied to the copals: Kauri, Borneo, and Manila copals are to the greater part soluble in 96% alcohol. White and yellow Benguela copal, red Angola, Congo, and Cameroon copals can be brought more or less into solution by first heating to 100° for 48 hours, powdering, then mixing with sand or powdered glass, allowing to stand with ether in which they swell, then adding the necessary quantity of warm alcohol. Sierra Leone and Zanzibar copals require long digestion. Manila copal, after it has been powdered and exposed, dissolves in ether; 40% of Sierra Leone copal dissolves in alcohol, but Zanzibar copal is scarcely affected. Spirits of turpentine has no immediate action on these resins, but when oxidised turpentine is used all copals are dissolved more or less, and Sierra Leone copal completely. Amyl acetate is a good solvent for these resins, but its use is marred by its odour. Amylic alcohol is a very active solvent for Kauri and Manila, but it scarcely affects the harder varieties. Alkaline solutions attack all copals—soft

varieties are easily saponified at a low heat, while the harder sorts are strongly attacked. Angola copal is completely dissolved.

Analytical Data.—Many workers have attempted to determine analytical limit constants for the copals, but as yet the values obtained have varied within such wide limits that the results cannot be employed in their commercial valuation.

Lippert and Reissiger (*Zeits. angew. Chem.*, 1900, **13**, 1047; obtained the following results in the analysis of various commercial samples. For the determination of the acid value, 1 grm. of the sample was treated with 10 c.c. of chloroform, and after standing some hours 25 c.c. of alcohol was added. If the copal was not dissolved by this treatment, ether, or a mixture of alcohol and ether, was used, and when solution was complete, the liquid was titrated with N/2 alcoholic potassium hydroxide, using phenolphthalein as indicator. The saponification value was obtained by heating the copal with alcohol and ether (not chloroform), adding excess of standard alcoholic potassium hydroxide, and proceeding as usual. The ester number is the difference between the acid and saponification values. In certain cases, such as Manila copal, it probably represents lactonic compounds and not esters.

Variety of copal	Acid value	Saponification value	Ester value	Remarks
Angola, white	59 to 61			R. Williams[1] found acid value 57.
Angola, red	90	148 to 152	58 to 62	Schmidt and Erban[2] found saponification value 148.
Angostura	48			Fine glassy yellow lumps.
Benguela, select	61 to 62	111 to 126	50 to 64	Clear yellow balls.
Benguela, ordinary	84 to 87			Contains dirt.
Brazil, select	153 to 158	148 to 157	1 to 5	Splendid pale yellow balls.
Cameroon	106 to 109			Easily soluble in alcohol.
Dammar	33 to 35			Completely soluble in oil of turpentine.
Kauri, select	81			Not quite transparent.
Kauri, light ordinary	63 to 64	95 to 109	32 to 39	Williams found saponification value 64.2.
Kauri, dark	66.5 to 70			
Madagascar	60			Easily soluble in alcohol-chloroform.
Manila, select	103 to 111	147 to 152	43 to 50	Hard, easily soluble in alcohol.
Manila, soluble in alcohol	144 to 148			Soft, easily soluble in alcohol.
Sierra Leone	78 to 82			Small light balls.
Zanzibar		88 to 102		Characteristic "goose-skin" appearance.

[1] Williams' results will be found in detail in *Chem. News*, (1888), **58**, 224.

[2] Schmidt and Erban's results are recorded in *Zeits. angew. Chem.*, 1889, **1**, 35. Coffignier has published further constants and solubility values for Zanzibar and Madagascar copals (*Bull. Soc. Chem.* 1903, **29** (ii), 581).

.tigators[1] have obtained values differing widely from those given in the above table. It is very probable that the varying n   /ed in the determination of the values may partly .   discrepancies, but the complex composition of the copals, and the doubtful relationship existing between the name and origin of the commercial resins, affords the more probable explanation.

J. Marcusson and G. Winterfeld suggest the following method for the determination of the acid value: 3 to 4 grm. of the finely powdered resin are heated for a short time with 200 c.c. of a mixture containing equal parts of benzol and neutral absolute alcohol. When cold the solution plus any undissolved resin is titrated with $N/10$ alcoholic potassium hydroxide in the presence of phenolphthaleïn.

They obtained the results given on p. 9 by this process.

R. A. Worstall has published some valuable results obtained with the fossil resins (*J. Amer. Chem. Soc.*, 1903, **25,** 860). He ascertained the "acid" value by Dieterich's indirect process. The iodine values obtained by this observer (by treating 0.2 grm. of the sample and 10 c.c. of chloroform with 50 c.c. of Hübl solution for 18 hours in the usual way) were as follows:—

Copal	No. of samples examined	Iodine value	
		Max.	Min.
Kauri	43	170	74
Manila	19	148	104
Pontianac	2	142	119
Zanzibar	2	123	115
Mozambique	1	136	
Madagascar	1	126	
West African	8	143	122
Sierra Leone	2	105	102
Brazilian	3	134	123

Schmidt and Erban (*Zeit. angew. Chem.*, 1889, **1,** 35) found, in the case of *melted* Angola copals, 93.6 and 25.2 for the acid and ester numbers, respectively, of the white variety, and 30.5 and 89.2 for the same

[1] Coffignier, "Properties of Several African Copals." *Revue de Chimie industrielle,* **16,** 103–106.
    Coffignier, "Several American Copals." *Bull. Soc. Chim.,* 1906, [3]. **35,** 1143.
    Coffignier, "Manila Copals," etc. *Bull. Soc. Chim.,* 1907, [4] **3,** 453.
    Tschirch and Engels, "Congo and Benguela Copals." *Archiv. Pharm.,* 1908, **246,** 293–305.
    R. A. Worstall, *J. Amer. Chem. Soc.,* 1903, **25,** 860.

constants of the red variety. The iodine absorption of the white
Angola copal was 44.9 and 34.8 for the red variety. Hirschsohn gives
91 as the saponification number of unmelted Zanzibar copal, the
melted resin having a value as low as 35.7. For Angola copal he
gives 131 to 147.3 for the unmelted and 110.2 to 120.3 for the melted
resins.

Anime resin is of somewhat variable and, in many cases, doubtful
origin. It appears in general to be closely related to elemi and copal,
and is usually the product of species of *Bursera*. Anime is frequently
known in English commerce as *soft copal*, while Madagascar copal is
known in France as *anime*. The so-called East and West Indian anime
is the product of *Hymenæa coubaril*, and the same name has been
applied to resins from various other sources.

The chemistry of anime resin· is naturally but little understood.
Anime appears to contain a large amount of essential oil, which, accord-
ing to Paoli, is sometimes present to the extent of 24%.

A sample of anime examined by E. Dieterich contained 54.3%
of resin soluble in cold alcohol, and 43% of resin soluble in hot (but
insoluble in cold) alcohol.

The analytical figures which have been recorded for this resin will be
found on page 12.

SANDARAC.

Occurrence.—This resin is the natural exudation from *Callitris
quadrivalvis (Coniferæ)* and allied species. Occasionally Australian
sandarac known as "pine-gum" or white pine resin" is found on the
market.

Chemical Composition.—A. Tschirch and M. Wolff (*Archiv.
Pharm.*, 1906, **244**, 684) have found that when sandarac is submitted
to Tschirch's systematic scheme for the examination of the resins it
yields sandaracinic acid, $C_{22}H_{34}O_5$, which softens at 180° and melts at
186° to 188°; sandaracinolic acid, $C_{24}H_{36}O_3$, which has no sharp m. p.,
but fuses from 265° to 275°; sandaracopimaric acid, $C_{42}H_{30}O_2$ (identical
with Henry's *i*-pimaric acid) which is crystalline and forms flattened
rosettes, m. p. about 170°; and a resene, sandaraco-resene, $C_{22}H_{36}O_2$.
In addition to these resins and volatile oils, sandarac contains a bitter
principle.

According to Henry, the essential oil contains dextro-pinene and a
diterpene boiling at 265°.

Uses.—This resin is an important constituent of many spirit varnishes, *e. g.*, label varnishes, negative varnishes, etc.

Adulterants.—Sandarac is sometimes adulterated with colophony, and at times with some varieties of cheap dammar.

General Properties.—This resin generally occurs in the form of grains varying from ρ.5 to 1.5 cm. in diameter; it is also found in short cylindrical pieces at times aggolomerated together, while the finest varieties consist of clear yellow drops. The surface of the grains has a dusty appearance. This resin is somewhat harder than mastic; when chewed it does not agglomerate.

Specific Gravity.—This value varies between 1.05 and 1.092.

Melting Point.—Sandarac liquefies at 160°.

Solubility.—Sandarac is soluble in alcohol, ether, amyl alcohol, acetone, and in several ethereal oils. · Chloroform, turpentine, and fatty oils dissolve it partly; in benzene, carbon disulphide, and petroleum ether it is difficultly soluble, while glacial acetic acid hardly affects it. Hirschsohn found from 7 to 8% of sandarac to be soluble in petroleum ether, and Mauch states that about 5% is soluble in 60% chloral hydrate solution.

Analytical Data.—The acid value is of importance in the examination of this resin, and K. Dieterich has suggested the following indirect method for its estimation.

Acid Value (Indirect).—1 grm. of sandarac is suffused with 20 c.c. of N/2 alcoholic potassium hydroxide and 50 c.c. of benzin (sp. gr. 0.700), and left to stand for 24 hours in a tightly closed vessel, at the end of which time the contents are titrated back with N/2 sulphuric acid, without the addition of water. The c.c. of standard KOH combined multiplied by 28.02 gives the acid value.

The following analytical characters have been recorded:

Observers	Moisture; %	Ash; %	Acid number	Acetylated resin	
				Acid number	Ester number
E. Dieterich			97 to 123		
K. Dieterich			90 to 110	166 to 170	74 to 82
A. Kremel			144		
Von Schmidt and Erban			140	140	
R. Williams	0.04; 0.17	1.9; 1.4	154; 146		

⸿MASTIC.

Occurrence.—Mastic is the product of *Pistacia lentiscus*, one of the Anacardiaceæ.

Commercial Varieties.—Chios mastic is the kind most generally used and the most prized variety; East Indian or Bombay mastic is also known in commerce.

Chemical Composition.—The chemistry of mastic is very little understood, but Flückiger isolated from it 2% of an essential oil, which consisted chiefly of a slightly dextrorotatory terpene. Tschirch and Reutter (*Arch. Pharm.*, 904, **242,** 104) found Chios mastic (acid number 59 and saponification number 82.5) to contain: α- and β-masticic acids, 4%; masticolic acid, 0.5%; masticonic acids, α 20%, β 18%; mastico-resenes, α 30%, β 20%; essential oil, 2%; bitter-substance, impurities, etc., 5.5%. (See also tables on pp. 5 and 6.)

Uses.—This gum finds some application in lithographic work. The extreme paleness of the varnish makes it suitable for coating white metallic objects and pictures.

Adulterants.—Mastic is sometimes adulterated, especially when in powder, with sandarac, colophony, and other pine resins.

General Properties.—The grains of Chios mastic have a long or ovoid shape, varying from 0.5 to 2 cm. in diameter. Bombay mastic sometimes occurs in large irregular pieces, also in the same form as Chios mastic. The grains are always more or less milky, and have a dull appearance due to minute superficial fractures. The colour is yellow or greenish, and the taste and smell reminds one of turnips. When chewed mastic gives a doughy mass; all other resins with which it is likely to be adulterated fall to a powder.

Specific Gravity.—Pfaff gives the sp. gr. at 1.04, while Schrötter and Brisson give 1.07.

Melting Point.—Böttler states that poor-quality mastic softens at 85° to 93°, and melts at 103°, while the better qualities soften at 99° and melt at 108°. Johnson gives the m. p. at 100°, whereas Schrötter states that it softens at 80° and melts with partial decomposition between 105° and 120°.

Solubility.—Mastic is completely soluble in 80% chloral hydrate solution, and, according to von Schmidt and Erban, is partially soluble in alcohol, methyl alcohol, acetone, acetic acid, chloroform, and oil

of turpentine; slightly soluble in carbon disulphide; completely soluble in ether, amyl alcohol, and benzene, and insoluble in petroleum ether. Chios mastic is soluble to 75% in benzine sp. gr. 0.700, whereas the Indian variety is only soluble to the extent of 10%. Indian mastic when dissolved in turpentine gives a varnish which hardens extremely slowly, whereas a quick drying varnish is obtained from Chios mastic.

Analytical Data.—The following figures have been recorded for genuine samples of mastic:

	A. Kremel	R. Williams	Von Schmidt and Erban
Acid number.......	$\begin{cases} 61.8;\ 70.9 \\ 67.2\ \text{(E. Dieterich)}. \end{cases}$	50.04; 56.0	64.0
Ester number.....	....	23.00; 23.10	29.9
Ash, %..	....	0.21; 0.14	
Water, %........	....	0.97; 1.46	

The United States Pharmacopœia (8th Rev.) requires for mastic an acid number of not less than 65.

Detection of Adulterants.—The high acid value obtained when sandarac colophony and other pine resins are present as adulterants will indicate the presence of these bodies.

DAMMAR RESIN.

Occurrence.—The chief variety of this resin which occurs in commerce is in all probability the product of a variety of *Hopea*, one of the *Dipterocarpeæ;* but other plants are said to have produced much of the resin, such as species of *Vatica, Dryobalanops, Doona,* and *Vateria*.

Commercial Varieties.—The East Indian dammars, obtained from Java, Singapore, and Padang, are the only kinds which are of importance for the European markets; besides these white dammars there are several descriptions of dark and black resins collected in India, but these varieties are not used commercially in Europe.

Chemical Composition.—The constituents of dammar resin which have so far been identified (G. Glimman, *Archiv Pharm.,* 1896, **234,** 584) are as follows: dammarolic acid, $C_{54}H_{77}O_3(COOH)_2$, which is present to the extent of 23%; α-dammarresene, $C_{11}H_{17}O$ (40%, soluble in alcohol); β-dammarresene, $C_{31}H_{52}O$ (22.5%,

insoluble in alcohol); ethereal oil and a bitter substance, 0.5%; water, 2.5%; ash, 3.5%; and undefined impurities, 8%.

B. Graf (*Archiv Pharm.*, 1889, **227**, 97) examined 5 samples of East Indian dammar and found about 1% of a free dibasic acid having the formula $C_{18}H_{33}O_{3}$. Of the other portion of the resin 40% was insoluble and 60% soluble in alcohol. The soluble portion was described as m. p. 61° and having the formula $C_{20}H_{42}O_{2}$. The insoluble portion contained oxygen and m. p. 144° to 145°. No hydrocarbon could be detected.

Uses.—This resin is extensively used in the varnish industry; the so-called "crystal varnishes" consist chiefly of dammar dissolved in oil of turpentine.

Adulterants.—The powdered material is often adulterated with colophony; Kauri copal is also a frequent adulterant.

General Properties.—Singapore dammar is found in commerce in the form of nodules varying in size from 0.5 in. to 1.5 in. in diameter, sometimes larger, covered with a powdery crust. The material is usually clear and transparent. It is either colourless or at most a faint straw tint. It is friable and breaks easily with a powdery fracture. Batavian dammar has the highest commercial value on account of its perfect colour and the fact that it does not yield a milky solution when dissolved in turpentine.

Specific gravity varies from 1.062 to 1.123.

Melting Point.—The resin softens at 75°, becomes syrupy at 100°, and at 150° is clear and thin. When subjected to destructive distillation dammar resin yields an oil.

Oil of dammar resin has a golden-yellow colour and a bitter taste. According to H. Haensel, it has a sp. gr. at 21° of 0.9552. It is optically inactive and boils between 205° and 265°. 60% of the oil distils below 240°, this fraction having a sp. gr. of 0.9175. It is soluble in most organic solvents.

Solubility.—Dammar is partly soluble in methyl and ethyl alcohols, ether, acetone, and glacial acetic acid. The Batavian dammars dissolve more readily than the other varieties. Benzol, chloroform, carbon disulphide, sulphuric acid, and oil of turpentine dissolve the resin completely. E. Hirschsohn has examined a large number of samples of dammar and found that, with the exception of *Dammar marmoratus*, all the specimens yielded from 73 to 80% of extract to petroleum ether, and from 57 to 87% to alcohol of 85% strength.

80% chloral hydrate solution causes the dammar to swell, but only a very small quantity is dissolved after months of standing.

Analytical Data.—The analytical figures for this resin will be found in the table on page 12.

Acid Value.—K. Dieterich has shown that with this resin the direct estimation of the acid value gives low results, so he has proposed the following empirical method for its indirect valuation.

1 grm. of dammar is suffused with 50 c.c. of benzine, sp. gr. 0.700, 20 c.c. of N/2 alcoholic potassium hydroxide is then added. The whole is allowed to stand 24 hours and is then titrated with N/2 sulphuric acid and phenolphthaleïn without the addition of water. The acid value (indirect) is the product of the c.c. of KOH multiplied by 28.02.

K. Dieterich has given 20 to 30 as the limit figures (indirect) for this constant.

Detection of Adulterants.—E. Hirschsohn (*Zeit. anal. Chem.*, 1898, **37**, 456) states that 5% of colophony can be detected in dammar resin by digesting the sample for half an hour with solution of ammonia (sp. gr. 0.960) and acidifying the filtered liquid with acetic acid. In the presence of colophony, a precipitate of resin acids is formed, whereas pure dammar yields a faint opalescence, since only traces of the acid of dammar resin are extracted by ammonia. The comparative insolubility of dammar in 80% chloral hydrate differentiates it from the conifer resins and softer copals, which are soluble in this medium.

An acid value (indirect) higher than 30 would point to the presence of colophony as an adulterant.

DRAGON'S BLOOD.

The chief variety of dragon's blood is the "Palm dragon's blood," from *Dæmonorops draco*.

Commercial Varieties.—The resin obtained from Sumatra is the only one of commercial importance. K. Dieterich (Helfenberger Annalen, 1903) has investigated the resin obtained from Socotra and from the Canary Islands, but these resins have no technical importance.

Chemical Composition.—Tschirch and K. Dieterich found in the resin from *dæmonorops draco* about 18% of insoluble plant substances; 2.5% of *dracoalban*, $C_{20}H_{40}O_4$, obtained by the addition of alcohol to the ethereal solution of the sample; about 14% of *dracoresene*,

$C_{20}H_{44}O_2$; and a red amorphorus powder, which after purification melts at 72°, obtained by evaporating the filtrate from the dracoalban to dryness and extracting the residue with petroleum ether. This last substance appears to be a mixture of the benzoic and bezoyl-acetic esters of an alcohol, *dracoresinotannol*, $C_8H_{10}O_2$. Socotra Dragon's Blood, from *Dracæna cinnabari*, a variety not used to any considerable extent, appears to contain esters of both benzoic and cinnamic acids, but no dracoalban.

Uses.—This resin is used in the preparation of red spirit varnish. It is one of the best colouring matters that can be employed for this purpose.

Adulterants.—Colophony is employed in adulterating the lump dragon's blood. In addition to colophony, oxide of iron, Armenian bole, red sanders, and various gums are said to have been used.

General Properties.—This resin is sold in the form of roughly cylindrical sticks about 13 to 14 in. long and about 0.75 in. to 1 in. thick; smaller pieces are not uncommon. It is also sold in the form of balls the size of olives. This is the best variety. A second quality is sold in plates, and a third quality in large pieces. This resin shows various colours according to the quality. The surface is blackish-brown with a deep red fracture. The qualities of lesser value have a deep sealing-wax red appearance. All varieties are opaque, have a sweet taste, and the resin portion falls to a powder when the material is chewed. A good quality dragon's blood must be clear, and when crushed a carmine-coloured powder should be obtained, which dissolves in spirit with a deep red colour. When dissolved in alcohol a good-quality resin only leaves a residue of about 9%, principally vegetable fibre and sand. The less valuable varieties often give 20% of residue.

Specific Gravity.—The finer qualities of resin have a sp. gr. of 1.2; the less valuable varieties slightly under this figure.

Solubility.—In alcohol and ether this gum is readily soluble, whereas it is only partially dissolved by chloroform, ethyl acetate, petroleum ether, and carbon disulphide.

Identification and Analytical Data.—The following test for distinguishing palm dragon's blood from other varieties has been proposed by K. Dieterich (Analysis of Resins, etc., page 154); 10 grm. of powdered dragon's blood should be extracted with 50 c.c. of hot ether, filtered from woody fibre and other insoluble matter, the solution con-

centrated to about 30 c.c., and the whole then poured into 50 c.c. of cold absolute alcohol. After standing for 1 hour, a white flocculent precipitate of dracoalban, soluble in most organic solvents, but insoluble in alcohol, will be formed if palm dragon's blood be present. Other varieties of the resin are said not to contain this resene. A sample of palm dragon's blood adulterated with colophony, etc., will only respond very slowly to this test.

K. Dieterich (*Chem. Rev. Fett-Harz-Ind.*, 1897, [4], 207) has suggested the determination of the resin value and the gum saponification value for the valuation of dragon's blood, for which he has given the following limit figures:

Resin value H. Z........... 79.8 to 119.0 ⎫ Palm dragon's
Gum saponification value.... 86.8 to 173.2 ⎭ blood.

Very large quantities of colophony could be present in dragon's blood without causing these values to exceed the higher limit figures, so at present these values are only useful in certain cases.

Gregor and Bamberger found the methoxyl numbers of three samples of dragon's blood to be 27.6, 25.3, and 33.8. R. Williams found a good commercial sample to contain 9.34% of water and 3.6% of ash. K. Dieterich found 8.3% of ash. The acetyl number of palm dragon's blood was found by K. Dieterich to be about 140.

Detection of Adulterants.—Artificial dragon's blood, consisting of colophony mixed with sealing wax, red ochre, and a small quantity of real dragon's blood, when crushed, gives a dull red, not a bright red, powder. When heated it emits an odour similar to that of colophony.

GUAIACUM.

Occurrence.—This resin is obtained from the stem of *Guaiacum officinale* and *G. sanctum* of tropical America.

Chemical Composition.—According to Döbner and Lücker (*Archiv Pharm.*, 1896, **234**, 590), guaiacum contains about 11% of *guaiaretic acid* (guaiacum resin), $C_{20}H_{23}O_3(OH)$, crystallising in white lustrous laminæ, m. p. 86°; 50% of *guaiaconic acid*, $C_{20}H_{22}O_3$-$(OH)_2$, a white amorphous powder, m. p. 75° and soluble in ether; 12% of *guaiacic acid*,[1] $C_{21}H_{19}O_4(OH)_3$ (the β-resin of Hadelich),

[1] The chemistry of guaiacum is of especial interest on account of the synthetic experiments of Döbner, who succeeded in obtaining resin acids closely resembling those of guaiacum. By the condensation of tiglic aldehyde, guaiacol, and cresol, Döbner obtained a brown resin having the composition $C_{20}H_{24}O_4$, which is therefore isomeric with guaiaretic acid. From

insoluble in ether; a yellow crystalline substance, "guaiacum yellow," $C_{20}H_{20}O_7$, m. p. 115°, and soluble in strong sulphuric acid with deep blue colouration; about 10% of gum; 2% of ash; and undefined matters and loss.

Uses and Adulterants.—Guaiacum is used to a considerable extent in medicines. The mass variety varies greatly in quality, and the commoner kinds frequently contain a considerable quantity of woody fibre. Apart from this impurity which may be regarded as an adulteration, when present in excessive amount, guaiacum sometimes contains an admixture of colophony, and it is also said to be mixed abroad with another species of resin unknown in commerce.

General Properties.—Guaiacum occurs in rounded tears and in masses of a green or brownish-green colour. It is a glassy, brittle solid, having a somewhat reddish fracture when fresh, but which darkens to green. Its odour and taste are very slight, but on chewing the resin a burning sensation is imparted to the throat. Guaiacum melts at about 85°.

Solubility.—Rabenau found from 54 to 74% of guaiacum to be soluble in ether. Very small quantities of guaiacum are soluble in petroleum ether, up to about 4.0%, after drying the residue at 120.°

Identification and Analytical Data.—Numerous oxidising agents produce a blue colour when brought into contact with tincture of guaiacum, and this property is the basis of several useful reactions, as, for instance, in detecting the presence of blood (Vol. VIII). The colouration is due to the action of oxygen upon guaiaconic acid, the resulting compound probably having the formula $C_{20}H_{20}O_6$. Döbner recommends that the pure acid itself, and not the mixture of acids obtained from a tincture of guaiacum, should be used in such tests.

The proportion of alcohol-soluble matters and of ash in guaiacum are the most important factors in its examination. Ward found the ash in three samples to range from 3 to 6.8%, the matter soluble in alcohol from 87 to 96%, and the matter soluble in water from 3 to 4.7%. John Evans found the matter soluble in alcohol in 6 samples to

a study of the reaction in which it **is** formed, the constitution of the synthetic product is stated to be:

$CH(CH_3): C(CH_3).CH[C_6H_2.(CH_3.)(OCH_3.)OH].C_6H_3(OCH_3).OH.$
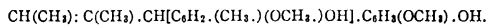
In a similar way, by condensing tiglic aldehyde with guaiacol and the dimethyl ether of pyrogallol, an acid isomeric with guaiaconic acid was obtained, and by using only tiglic aldehyde and the dimethyl ether of pyrogallol, an acid having the formula $C_{21}H_{24}O_6$ was obtained. These results have strengthened the hypothesis that many of the resins are formed in nature by the condensation of substances of aldehydic and phenolic character rather than by the oxidation of terpenes.

range from 90.0 to 98.5%, the amount of ash in the insoluble matter being very variable, and ranging from 11.5 to 56.2%.

Acid Value (Indirect).—The following special method for the estimation of this value is due to K. Dieterich. 1 grm. of resin is suffused with 10 c.c. of N/2 alcoholic potassium hydroxide and 10 c.c. of N/2 aqueous potassium hydroxide and left for 24 hours in a flask fitted with a glass stopper. After adding 500 c.c. of water, the liquid is titrated back with N/2 sulphuric acid and phenolphthaleïn. The following figures for guaiacum have been recorded:

Observer	Acid number	After acetylation	
		Acid value	Ester value
A. Kremel...............	23 to 44		
K. Dieterich............	....	{ Mass variety, 46 to 53 { Purified by } 13.6 to { Alcohol } 13.9	122 to 139 149 to 150

The acid values after acetylation are widely different in the case of the mass variety and of the purified guaiacum, but no explanation of the discrepancy is offered by Dieterich. Guaiacum contains mere traces of esters only.

The methoxyl number of guaiacum ranges from 74 to 84 (Gregor and Bamberger).

Detection of Adulterants.—For the detection of colophony in guaiacum, the Storch-Morawski reaction may be employed (see Colophony). Hager states that this adulterant may be detected by adding excess of potassium hydroxide solution to an alcoholic solution of guaiacum. An insoluble resin soap will be precipitated in the presence of colophony. The potassium salt of guaiaretic acid is, however, precipitated from guaiacum by this method (Döbner).

Hirschsohn states that the presence of either colophony or of a foreign species of guaiacum, such as the so-called Peruvian guaiacum (*Guaiacum peruvianum odoriferum*), may be detected by adding a solution of bromine to a chloroformic solution of guaiacum. Pure guaiacum yields a blue colour, while an adulterated sample will give a red colouration.

SHELLAC.

Occurrence.—Shellac is the secretion of the lac insect, *Tachardia lacca* (*Coccidæ*) found on a large number of widely different plants, such as *Betua frondosa* and *Ficus religiosa*, and on certain other trees specially grown for the insect.

Commercial Varieties.—Crude "stick lac" contains much impurity such as dirt and woody fibre, while the crushed and washed lac, known as "seed lac" is correspondingly purer. The purified resin is the form in which most of the lac is sold, and is then known as "shellac." With insignificant exceptions all the "shellac" of commerce is manufactured in or about Calcutta, but a large amount of "button lac" is made both in England and in Germany. Numerous grades of shellac are recognised. The fine orange, which varies from a pale orange to a lemon-yellow colour, and the second orange grade of shellac, the latter being usually described as of T. N. in a diamond standard, should be and generally are pure. Numerous other grades follow these down to samples of very bad colour. Some of the dirty yellow shellac of commerce is arsenical, being coloured with a small quantity of orpiment.

Button Lac.[1]—Button lac, a form in considerable demand for certain purposes, is melted and poured so as to form large, round, flat pieces, which, owing to thickness, appear of a dark brown colour, but are ruby-red by transmitted light.

Garnet Lac.—Garnet lac is very similar to "button" lac both in colour and appearance. It is made into thick, flat irregular pieces. White or bleached shellac occurs in twisted masses resembling "peppermint rock."

Chemical Composition.—The chemistry of shellac has been but incompletely studied, though a few well-defined constituents have been recognised. In addition to accidental impurities, such as water (up to 4%) and small quantities of sand, woody fibre, etc., shellac contains *wax*[2] in proportions varying from traces up to about 6%. There is also usually from 2 to 6% of laccin pigment present, and a small quantity of *laccainic acid*, $C_{10}H_{12}O_8$, which forms an important constituent of lac dye, and is a substance closely allied to the colouring

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[1] It is stated on reliable authority that not more than about 1400 chests of pure button lac, absolutely free from added rosin, are imported into Great Britain annually.

[2] Shellac wax melts at 50°, and consists of a mixture of equal parts of free alcohols (chiefly myricyl and ceryl alcohols) and of the stearic, palmitic, and oleic esters of these alcohols (Benedikt and Ulzer).

matter of cochineal.   The resinous matter of shellac ranges from 75 to
85%, and was prepared by A. Tschirch by exhausting crushed shellac
under a reflux condenser with petroleum ether to remove the wax and
then repeatedly treating the dried residue with warm water until the
liquid was no longer coloured, an additional 6.5% being thus removed.
Of the resinous matter thus purified 35% was dissolved by ether, and
consisted of traces of higher fatty acids, a yellow colouring matter
called *erythrolaccin*, $C_{15}H_{10}O_5 + H_2O$ (apparently a hydroxy-methyl-
anthraquinone), a small quantity of a crystalline odoriferous sub-
stance, and compounds apparently of the nature of *resenes*.   The
65% of shellac resin not dissolved by ether consisted chiefly of the
aleuritic ester of a very unstable *resinotannol*.   *Aleuritic acid* itself,
$C_{13}H_{26}O_4$, crystallises from aqueous alcohol in rhombic leaflets, or
from water or chloroform, in needles melting at 101.5°.

Uses.—Shellac is used very largely in various industries, notably
for the preparation of a certain class of polishes and varnishes, and for
the stiffening of hats and certain textile materials.   It is also a con-
stituent of sealing-wax, marine glues, and some kinds of cement.

Adulterants.—Shellac is an article of considerable value, and its
price is very variable, hence it is extensively adulterated, the usual
admixture being common rosin.   The second orange quality of shellac
in times of scarcity is very often adulterated with 1 to 5% rosin.   Gar-
net lac is invariably a mixture of shellac and rosin, usually containing
about 10 to 12% of rosin, and button lac is almost invariably adulter-
ated with the same material.   At times acaroid resin is employed
in the adulteration of shellac.

General Properties.—Shellac varies in colour from white to red,
the white and paler varieties are produced by bleaching or partly
bleaching the natural shellac.

Specific gravity varies from 1.113 to 1.214.

Solubility.—Tschirch states that shellac resin is almost entirely
soluble in methyl and ethyl alcohols, acetic acid, alkalies, and solution
of borax; only partially soluble in ether, ethyl acetate, chloroform,
acetone, and carbon disulphide; and almost insoluble in benzene,
toluene, and petroleum ether.

Von Schmidt and Erban find shellac to be soluble in methyl, ethyl,
and amyl alcohols and in glacial acetic acid; but insoluble or nearly
so in ether, acetone, petroleum ether, carbon disulphide, and oil of
turpentine, and only partially soluble in chloroform.   According to

Mauch, on treating shellac with an 80% aqueous solution of chloral hydrate it first swells up and then dissolves almost entirely.

It has been pointed out by Ulzer and Defris that shellac resin acids behave quite differently to the resin acids of colophony in Gladding's or Twitchell's process, and that the former appear to be more nearly related to the fatty acids than to the resin acids of colophony. (See Vol. 2 and *J. Soc. Chem. Ind.*, 1897, **16**, 364.)

On treating shellac previously dried at 120° with petroleum spirit, Hirschsohn found from 0.4 to 6.3% to pass into solution. These figures probably represent the proportions of wax present in the samples examined.

The ready solubility of shellac in hot aqueous solutions of potassium and sodium carbonates, alkaline hydroxides, and borax is well known, and this property is utilised in several ways. On the one hand, it is made use of in the preparation of the so-called water varnishes employed in the finishing of leather and, on the other hand, for the production of bleached shellac and of shellac soluble to a clear solution in alcohol. The shellac remains unchanged in these alkaline solutions and dries to a hard coat. It can be precipitated from the solution by an acid.

Benedict and Erlich have observed that shellac is largely converted by dilute alkalies into a balsam-like mass, described by them as "*liquid shellac.*" This is prepared by boiling 10 parts of shellac (previously freed from wax) with a solution of 3 parts of sodium hydroxide in 20 of water, acidifying the cooled mass with sulphuric acid, and extracting with ether. The ether is distilled, the residue (amounting to about 70% of the wax-free resin) consisting of the " liquid shellac." The product is probably little more than shellac resin hydrolysed, and containing a considerable proportion of water (Parry). By mixing liquid and ordinary shellac, plastic masses of any degree of softness can be obtained.

Identification and Analytical Data.—For the detection of colophony in shellac, E. J. Parry dissolves the sample in a little alcohol and pours the solution into water. The impalpable powder is collected on a filter-paper, dried, and then rubbed for some time with petroleum ether. The filtered liquid is next shaken with a little water containing a trace of copper acetate, when the petroleum ether will be coloured emerald-green if rosin be present, but in its absence will be quite colourless. As little as 5% of colophony may be detected by this

test, which is recommended by ℟ C. Umney as being most
satisfactory.

The Storch-Morawski test (page 28) with careful working gives indi-
cations which are extremely reliable.   With a large amount of
practice it is possible to differentiate between a rosin-free lac and one
containing 2½% to 3% of rosin.

The sp. gr. of a sample of shellac has been suggested as affording
an indication of the proportion of rosin present, but the densities of
the two resins are too variable and too nearly alike to render the test
of value.

E. J. Parry has pointed out (*Chem. and Druggist*, Oct. 26, 1901,
page 689; 1902, page 670; Jan. 31, 1903, page 175; 1905, page 556)
that the determination of the iodine absorption of the sample by Hübl's
process affords the most ready and accurate means of ascertaining the
proportion of colophony in adulterated shellac, the iodine figure for
shellac being remarkably low, while that for the adulterant is excep-
tionally high.   The iodine solution should be present in large excess
(100%) and should be allowed to act for 18 hours in the dark.   If
the deduction from the result be confirmed by the acid and ester
numbers of the sample, a very fair approximation to the true amount
of colophony present can be obtained.   Parry gives the following
figures obtained from the analysis of a large number of pure samples:

	Shellac	Colophony
Iodine absorption (%)	7.5 to 11 (average 9)[1]	125 (average).
Acid number	55 to 65 (average 60)	165 (average).
Ester number	150 (average)	0 to 6.

A. C. Langmuir (*J. Soc. Chem. Ind.*, 1905, **24**, 12) advocated the use
of Wijs' solution in determining the iodine value of shellac as a means
of estimating the proportion of rosin present.   The American Sub-
committee on Shellac Analysis (*J. Amer. Chem. Soc.*, 1907, **29**, 1221)
has accepted this method, with the addition of certain fixed conditions,
as a standard method for the estimation of colophony in shellac.

Standard Method.[2]—Introduce 0.200 grm. of ground shellac into a

[1] Parry states that the iodine absorption of arsenical lac sometimes reaches 14%.   J. C.
Umney prefers the value 10 as being the average iodine absorption (Hübl) of shellac, while
agreeing with Parry's figure 125 as the average iodine value for colophony.
[2] A solution of iodine monochloride in glacial acetic acid is required containing 13 grm.
of iodine per litre.   It is essential for accurate work that the glacial acetic acid be free
from reducing impurities, and the m. p. *must* lie between 14.7 to 15°.   A solution of sodium
thiosulphate is made by dissolving 24.839 grm. of the pure salt in 1000 c.c. of water.   In
addition to these solutions there is required a quantity of acetic acid of the same strength

250 c.c. dry bottle of clear glass with a ground stopper, add 20 c.c. of glacial acetic acid, m. p. 14.7°, and warm the mixture gently until solution is complete (except for the wax.) A pure shellac is rather difficultly soluble; solution is more rapid according to the proportion of rosin present. 10 c.c. of chloroform are then added and the solution is cooled to 21° to 24°. The temperature should be maintained well within these limits during the test. The 20 c.c. of Wijs' solution are added from a pipette having a rather small delivery aperture. The bottle is closed and stood in a dark place, and partly immersed in water which should be kept as nearly as possible between 22° and 23°. Pure shellac will scarcely alter the color of the Wijs' solution. If in small amount, rosin will produce a slowly appearing red-brown color. In large amount, rosin causes an immediate colouration, increasing in intensity as time passes. After 1 hour, 10 c.c. of 10% potassium iodide solution are added. The solution is immediately titrated with the sodium thiosulphate solution; 25 c.c. or 30 c.c. may be run in immediately unless the shellac is very impure, and the remainder gradually with vigorous shaking. Just before the end, a little starch solution is added. The end-point is sharp, as the reaction products of shellac remain dissolved in the chloroform; any colour returning after half a minute is disregarded.

A blank experiment should be made with 20 c.c. of Wijs' solution, 20 c.c. of acetic acid, 10 c.c. of chloroform, and 10 c.c. of 10% potassium iodide solution. The blank is necessary on account of the well-known effect of temperature changes on the volume and possible loss of strength of the Wijs' solution.

In the case of grossly adulterated samples it is necessary to use instead of 0.2 grm. of material, a smaller amount, say 0.15 grm. or even 0.1 grm., in order that the excess of iodine monochloride may not be too greatly reduced, as the excess of halogen is one of the factors in determining the amount of absorption. It is safe to say that in case less than 25 c.c. of thiosulphate solution are required, another test

as that used for making the solution of iodine monochloride. Pure chloroform and starch are also necessary. The preparation of the iodine monochloride solution presents no great difficulty, but it must be made with care and accuracy to obtain satisfactory results. There must be in the solution no sensible excess of iodine or more particularly chlorine over that required to form the monochloride. This condition is most satisfactorily attained by dissolving the requisite quantity of iodine in the whole of the acetic acid to be used, applying a gentle heat to assist the solution. A small portion of this solution is then set aside while pure and dry chlorine is passed into the remainder untill the halogen content of the whole of the solution is doubled. Ordinarily it will be found that by passing the chlorine into the main part of the solution until the characteristic colour of free iodine has just been discharged there will be a slight excess of chlorine which can be corrected by the addition of the requisite amount of the unchlorinated solution. A slight excess of iodine does little or no harm, but excess of chlorine must be avoided.

should be made, using a smaller amount of the shellac to be tested. In weighing shellac some difficulty is at times experienced on account of its electrical properties; in very dry weather it may be found that the necessary handling to prepare it for weighing has electrified it and that it may be necessary to leave it on the balance pan at rest for a few minutes before taking the final weight.

No pure shellac shows a higher iodine absorption than 18. This number has been adopted as the accepted standard for the method already described.

Different grades of rosin give iodine absorptions which vary from about 175 in the darkest varieties to 265 in the very pale sorts. Although theoretically any rosin might be employed for shellac adulteration, as a general rule the medium qualities with an iodine absorption of from 200 to 225 are used. The average iodine absorption number for rosin taken is 228. The result of taking 18 as the iodine absorption number of shellac and 228 for the iodine absorption value of rosin may be that, under some circumstances, a lower percentage of rosin will be found by this method than that actually present.

If $y = \%$ rosin
$M =$ iodine number of shellac
$N =$ iodine number of rosin
$A =$ iodine number of mixture

Then $Y = 100 \dfrac{A - M}{N - M}$

The treatment of shellac with alcohol and hydrochloric acid for the purpose of separating the oxy-acids has been recommended by H. Endemann (*Zeit. angew. Chem.*, 1907, **20,** 1776) for the valuation of commercial shellac.

2 grm. of the finely powdered sample are mixed with 4 grm. of very fine washed sand. 4 c.c. of alcohol and after a time 200 c.c. of concentrated hydrochloric acid are added. The mixture is stirred and evaporated to dryness on the water-bath. Alcohol and hydrochloric acid are again added to the residue, and the evaporation is repeated. After the contents of the basin have been heated in an air-bath for 2 hours at a temperature of 105°, the residue, when cold, is first moistened with a small quantity of hydrochloric acid, then with 20 c.c. of alcohol, and allowed to stand overnight. The solution is then poured through a filter and the filtrate is collected in a weighed flask and the residue is washed with successive quantities of alcohol until the filtrate measures about 150 c.c. The insoluble portion consists of wax,

myricyl alcohol, and condensed oxy-acids; it always retains chlorine and is unsuitable for weighing. The alcoholic filtrate is evaporated, and the residue is weighed after drying for 2 hours at a temperature of 102°. All acid compounds which do not belong to the oxy-acids are thus obtained. The best commercial shellacs contain about 87% of oxy-acids, 5% of wax, and 8% of soluble fat and resin, besides inorganic salts. If more than 8% of fat and resin be obtained the sample is either adulterated or inferior in quality. The results of the analysis can be expressed in terms of soluble resins above 8%.

The Acid and Ester Values of Shellac.—K. Dieterich made many experiments with mixtures of shellac and colophony and finally came to the conclusion that these values cannot be usefully employed in shellac analysis.

The following process for the estimation of colophony in shellac based on the method of Gladding and Twitchell for the separation of fatty and resin acids is recommended E. J. Parry. This method only gives good results when more than 20% of colophony is present. About 0.5 grm. of the sample is dissolved in the smallest possible quantity of alcohol and the solution cautiously treated with alcoholic potassium hydroxide till it is just neutral to phenolphthalein. This solution, containing the potassium salts of the shellac and resin acids, together with the neutral constituents of the shellac, is poured into about 100 c.c. of water contained in a separator, and about 0.5 grm. of silver nitrate, dissolved in a little water, added. The acids are precipitated as silver salts, and on shaking the liquid twice with ether, the silver salts of the resin acids of colophony are completely dissolved, while the silver compounds of the shellac acids remain insoluble. The ethereal solution is filtered, repeatedly agitated with water to remove silver nitrate, dilute hydrochloric acid added, and the liquid well shaken. The silver salts are decomposed, silver chloride being precipitated, and the resin acids recovered by evaporating the washed ethereal solution to dryness. The purity of the resin acids thus obtained may be verified by their iodine absorption. The above process only gives approximate results, the chief source of error being the slight solubility of a portion of the neutral constituents of shellac in ether, so that the results are rather higher than the truth.

White or bleached shellac occurs in twisted masses resembling "peppermint rock." It contains aleuritic acid, but no wax. It is prepared by dissolving ordinary shellac in an alkaline solution, pref-

erably sodium carbonate, and treating the liquid with chlorinated lime. Hydrochloric or sulphuric acid is then added, when the shellac is precipitated in a nearly colourless condition. The bleaching is due to the destruction or alteration of the erythrolaccin (p. 168). Bleached shellac, even when quite hard, usually contains a considerable proportion of water. It is not entirely soluble in alcohol, a substance resembling "lackstoff" being left as a residue. It is said to lose its solubility in alcohol very greatly by keeping, unless it is stored under water. In epichlorhydrin, bleached shellac is but sparingly soluble, and not much more so when the liquid is warmed; but in warm dichlorhydrin it is almost completely soluble. According to Tschirch, bleached shellac contains chlorine, so that the iodine absorption is materially modified. Rosin is usually added to this variety of shellac, notwithstanding the high estimation in which it is commonly held, but such adulteration is easy to detect, and an approximate estimation can be made.

OLEO-RESINS. TURPENTINES. BALSAMS.

The *oleo-resins* are a class of resinous exudations from plants, excreted naturally or obtained by tapping the trees. They consist essentially of mixtures of acid resins, resenes, and volatile oils, and rarely contain esters.

The name *turpentine* ought, strictly speaking, to be limited in its application to the oleo-resinous exudations from coniferous trees (*e. g.*, *Pinus*, *Abies*, *Juniperus*). It is, however, often applied to the spirit or essential oil (*e. g.*, oil of turpentine), obtained by distilling the crude turpentine, when the non-volatile resin is obtained as a secondary product.

Balsams are, correctly speaking, such of the oleo-resinous exudations of plants as contain benzoic or cinnamic acid and yield cinnamate or benzoate of methyl or ethyl by dry distillation. They are liquid, more or less viscous, and yield essential oils on distillation with water. The term balsam is misapplied to "Canada balsam" and "copaiba balsam," which are true turpentines not containing or yielding benzoic or cinnamic acid; while "dragon's blood" would be more properly classed among the resins.

The turpentines are viscous, honey-like liquids, or soft or brittle solids. Their odour is generally terebinthinate, but sometimes agree-

ably aromatic, and their taste varies from bitter, nauseous, and acid,
to a pleasant aromatic flavour.   The oleo-resins are not sensibly solu-
ble in water, though some yield traces of formic and probably succinic
acid to that solvent and, according to Tschirch, an alkaloidal
substance.

The description of the minute and often inappreciable differences
between the various oleo-resins known in commerce as turpentines and
balsams belongs rather to a work on pharmacy or materia medica than
to one on chemical analysis.   As their recognition and examination
are rarely required, it is unnecessary to describe the majority of them
in detail.[1]

Common Turpentine.

Common or American turpentine is the oleo-resin collected from
pine-trees growing in the Carolinas and other of the southern United
States.   The greater part of American turpentine is obtained from
the "longleaf" pine (*Pinus australis*).   The "loblolly" or "oldfield"
pine (*P. tæda*), the "pitch" pine (*P. rigida*), and the "swamp" or
Cuban pine (*P. cubensis*) supply comparatively small quantities only.
The crude turpentine is collected in pockets cut in the trees a few feet
from the ground.   The flow of the first year, called *virgin dip*, is the
best, and one barrel yields on distillation about six gallons of essential
oil and a residue known as *window-glass rosin.   Yellow dip*, the prod-
uct of the second and subsequent years, yields about four gallons of
oil per barrel, and furnishes the medium qualities of rosin.   The tur-
pentine which hardens on the trees is called *scrapes.*[2]   On distillation,
it yields about two gallons of oil per barrel and leaves a very dark
coloured (nearly black) rosin.

The essential oil obtained by the distillation of American turpentine
constitutes the oil of turpentine of commerce (which see).   The resin-
ous residue is known as colophony (page 21).

American turpentine was formerly distilled dry, but now an addition
of water is usually made, so that the oil may pass over in a current
of steam, and overheating be avoided.   The stills, which are of copper,

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[1] Much information on the origin, methods of obtaining, and characters of the turpentines
and balsams will be found in Hanbury and Flückiger's *Pharmacographia*, and in Watt's
Dictionary of Chemistry, **1,** p. 491 *et seq.*, and **8,** 1743.   A most exhaustive series of
articles by Julius Morel were published in the *Pharm. Journal* [3], **8,** pp. 21, 81, 281,
342, 542, 725, 886, 981, 1024; and **9,** pp. 673 and 714.
[2] *Thus americanum*, B. P., or common *frankincense*, is the concrete oleo-resin scraped
from the trunks of *Pinus palustris* and *P. tæda*.   The terebinthina (white turpentine) of
the U. S. Pharmacopœia is the same substance.   The name "frankincense" is also applied
to the resin of olibanum.

hold from 8 to 50 barrels. The vapour is condensed in a worm sur-
rounded with cold water, and the distillate flows into a tank, where
the oil collects on the surface. The resin which remains in the still
is run off while still fluid and constitutes the common *rosin* or *col-
ophony* of commerce.

Bordeaux or French Turpentine.

This product, also called *Gallipot* or *Barras,* is mostly the product
of *Pinus maritima,* but smaller quantities are obtained from the *Pin
franc,* or frankincense pine. In physical characters it closely resembles
American turpentine, but on distillation yields a lævorotatory oil and
a resin which contains *pimaric acid.*

Russian turpentine is the oleo-resinous exudation from the Scotch
fir, *Pinus sylvestris;* German, from the same species or from *P. rotun-
data;* Austrian, from *P. laricio;* Hungarian, from *P. pumilio;* Strass-
burg or Alsace turpentine is the product of the silver fir, *Pinus picea*
or *pectinata* (otherwise, *Abies excelsa*). It has an agreeable odour,
resembling that of lemon.

The following analytical data have been recorded for common
turpentines.

	Acid value	Ester value	Sapon. value
E. Dieterich:			
American............................	112–139	9.8–32.5	140–161
French..............................	105–141	2.8–9.8	109–149
Carpathian (*P. cembra*).............	117–119	56–60	167–179
P. sylvestris.......................	129–145	35–39	167–180
K. Dieterich.........................	107–116	4.1–20	115–134
Dietze: French.......................	120–120.4	1.8–3.0	121–123

More constant and reliable results would be obtained by first driving
off the essential oil in a current of steam, and determining the acid and
saponification numbers of the residue.

Venice Turpentine or Larch Turpentine.

Occurrence.—This product is the oleo-resin from *Larix Europœa* or
Pinus larix.

Chemical Composition.—Tschirch has recently studied the chemi-
cal constituents of larch turpentine (see page 80).

Uses.—This oleo-resin is largely employed for lithographic purposes, also as an ingredient for certain varnishes.

Adulterants.—Common turpentine and artificial products consisting of colophony, rosin oil, and oil of turpentine are often employed.

General Properties—Venice turpentine is a viscous liquid of a yellowish or greenish-yellow colour. Resin acids never crystallise out from this oleo-resin as is the case with some other turpentines. It has a characteristic smell and bitter taste, atributed by Flückiger to the presence of a glucosidal principle.

Solubility.—This oleo-resin is completely soluble in alcohol, ether, acetone, glacial acetic acid, chloroform, and turpentine, but is only partly dissolved by petroleum-ether.

Identification.—L. E. Andés recommends as a useful adjunct to the analytical values and the observation of the odour, inflammability, and solubility in 90% alcohol the following test, suggested by Hirschsohn, who has observed that ordinary turpentine, on treatment with 5 volumes of ammonia solution (sp. gr. 0.96), gradually yields a milky emulsion, while in the case of larch turpentine the liquid remains clear. When the lower layer of larch turpentine is stirred it is gradually transformed into a semi-solid, opaque substance, while the supernatant liquid becomes slightly turbid. Ordinary turpentine, however, is immediately distributed and the milky emulsion rapidly solidifies to a gelatinous mass. In the case of a mixture of the two in equal parts, the substance is distributed throughout the ammonia, and a solid mass, which clears on heating, is obtained in about 5 minutes. When the mixture only contains about 20% of ordinary turpentine, the milky emulsion becomes clear on heating the tube in boiling water, but no solidification occurs. Comparative tests with genuine larch turpentine may serve to detect smaller quantities.

Analytical Data.—The following analytical data have been recorded for Venice or larch turpentine:—

	Acid value	Ester value	Sapon. value	Iodine number
A. Kremel..................	68–70			
Von Schmidt and Erban.....	68	30	97	
Von Italie................	70	50	120	
E. Dieterich..............	64–77	35–56	108–133	
K. Dieterich..............	67–69	46–55	115–128	
A. Rudling...............	74	48	122	148

K. Dieterich has also recorded the following acetyl values for larch
and ordinary turpentine:

	Larch turpentine	Common turpentine
Acetyl-acid value	70–72	124–126
Acetyl-ester value	109–119	62–94
Acetyl-saponification value	179–191	188–217

Detection of Adulterants.—*a*. Rosin oil. To detect rosin oil
G. Fabris dissolves 5 grm. of the sample in 20 c.c. of 95% alcohol, and
adds a 10% solution of potassium hydroxide till the mixture is alkaline
to phenolphthaleïn. Venice turpentine thus treated yields a perfectly
clear solution, whereas the factitious turpentine containing rosin oil
becomes turbid, and on standing oily drops separate.

A factitious article, to which the name "Venice turpentine" is im-
properly applied, is made by mixing rosin, rosin oil and oil of turpentine.
It is employed in the manufacture of varnish and sealing-wax. Such an
article would necessarily give variable analytical figures, dependent on
the proportions of its constituents, but a mixture of the three substances
mentioned above would have a high acid number, a very low ester
number, and would contain a considerable proportion of unsaponifi-
able matter. Six samples examined by G. Fabris gave distillates
below 250° varying from 6.5 to 13%; acid values from 105 to 114;
and saponification values from 113 to 119. Genuine larch turpentine
is said to yield not less than 15% of essential oil.

A factitious Venice turpentine analysed by A. Rudling had an acid
number of 103; a saponification value of 117.6; and an iodine number
of 109.8.

A sample of so-called "Venice turpentine" examined in Allen's
laboratory by A. R. Tankard gave the following results: Acid num-
ber, 80.1; ester number, 7.73; saponification number, 87.8; unsaponi-
fiable matter (liquid, and gave reactions of rosin oil), 51.92%; essential
oil (volatile with steam), 3.0%; and optical activity of 10% alcoholic
solution of residual resin, +1.75° per 100 mm. It will be noticed that
these artificial products generally have the acid and saponification
value close together. When steam distilled, oil of turpentine can be
detected in the distillate, while a soft, sticky mass left in the distilling
flask denotes the presence of rosin oil. This can be separated after
saponification and detected by the usual methods.

b. Ordinary turpentine. Walbum (*Ark. Pharm. Kemi,* 1908, 105) has suggested the following method for the detection of this adulterant. 10 grm. of the turpentine are dissolved in 30 c.c. of ether; the solution is maintained at a *constant* temperature of 20.5° for 10 minutes. Then 8 c.c. of N/2 ammonia solution previously brought to the same temperature are added, and the mixture is well agitated. Pure Venice turpentine under these conditions sets to a jelly in 11 minutes, while in the presence of from 2 to 10% of ordinary turpentine, the gelatinisation takes place only after 12.7 to 26.8 minutes.

Hirschsohn (*Pharm. Zentralh.,* 1903, **44,** 845) recommends the following test for proving the presence of ordinary turpentine or an artificial substitute in Venice turpentine. 1 grm. of the material is treated with 3 grm. of 80% alcohol. If the solution is milky and a portion of the material is precipitated, then at least 10% of artificial or 30% of ordinary turpentine must be present.

Canada Balsam.

Occurrence.—This product, also known as balsam of fir, and balsam of Gilead, is the oleo-resinous exudation of the so-called balsam fir *Abies balsamea* and allied species.

Chemical Composition.—This turpentine contains 18 to 20% of oil, and 2 resins, one soluble in alcohol and the other difficultly soluble.

Tschirch[1] and his collaborators have described a large number of acids and resenes obtained from coniferous resins, but the formulæ and even the existence of many of the substances described require confirmation. The table on page 80 gives a résumé of their results.

Uses and Adulterants.—Canada balsam is used to a limited extent in medicines, in the preparation of flexible collodion and for mounting microscopic preparations. The usual adulterants of Canada balsam are colophony and common turpentine. Venetian turpentine[2] is sometimes added.

[1] According to A. Tschirch, with the exception of amber, all coniferous oleo-resins are free from esters, consisting solely of resin acids, resenes, and essential oil. These constituents may be separated as indicated on page 2. Only a few of the coniferous resin acids dissolve in ammonium carbonate solution. The majority are amorphous, are dissolved by sodium carbonate (1% solution), and may be separated by crystallisation or precipitation with lead acetate.

The resin acids of copaiba and Zanzibar copal, which are obtained from leguminous plants, present a close resemblance to the coniferous resin acids.

[2] A product known in commerce as "Oregon balsam" and consisting of a mixture of colophony and oil of turpentine much resembling Canada balsam is used as an adulterant of the latter substance (E. Dowzard, *Chem. and Druggist,* 1904, p. 439). The true so-called Oregon balsam is derived from *Pseudotsuga mucronata,* and its essential oil contains much lævo-pinene. Factitious Oregon balsam of the above composition contains the same proportion of resin as does Canada balsam, and their physical characters are almost identical. The presence of this adulterant is best detected by ascertaining the acid value of the essential-oil-free resin. Colophony has an average acid value of about 165, while that of the resin of Canada balsam averages 120 to 124.

COMPOSITION OF CONIFEROUS RESINS.[1]

	Strassburg	Bordeaux	Venice	Finland	Jura	Canada	Turpentine from	White pitch. (Russian "Beljivar")
Botanical origin	White fir, Abies pectinata.	Pinus mari-tima.	Larch, Larix decidua.	Pinus sylves-tris.	Picea vulgaris.[2]	Abies canaden-sis.	Pinus pal-ustris.	Abies pichta, or Abies sibirica.
Resin Acids. A. Soluble in Am. carbonate, amorphous.	Abienic, C_{11}-$H_{10}O_2$ (m. p. $114-115°$), K_1, cold, $9-10\%$.				Picea-pimari-nic, $C_{11}H_{20}O_2$ ($132-135°$), $2-3\%$, K_1, cold and boil-ing, I_1.	Canadinic, $C_{10}H_{14}O_2$ ($135-136°$), 13%.	Palabieninic, $C_{13}H_{20}O_2$, 5%. Sol. in Na_2CO_3, Palabieti-nic ($6-7\%$) (cryst.), $C_{20}H_{30}O_2$ ($153-154°$). Lævoro-tatory.	Beljiabien-nic, $C_{15}H_{22}$-O_2, $4-5\%$. Beljiabe-tinic, C_{20}-$H_{30}O_2$ (cryst.), ($2.5-3\%$).
B. Insoluble in Am. carbonate. a. Crystallisable.	Abietolic, C_{20}-$H_{28}O_2$ ($145-153°$), K_1, cold; K_2, hot, $1.5-2\%$.	Pimaric, $C_{20}H_{30}O_2$ ($144-146°$), $15-20\%$.	Laricinolic, $C_{20}H_{30}O_2$ ($147-148°$), K_1, more, with excess.	Silveolic, C_{15}-$H_{20}O_1$ ($138°$), K_1, cold and hot, 1.5%, I_1.	Picea-pimaric, $C_{20}H_{30}O_2$ ($144-145°$), K_1, cold and hot, I_1, $1.5-2\%$.	Canadolic, $C_{19}H_{28}O_2$ ($143-145°$), K_1, cold, K_2, (nearly) hot.		
b. Amorphous	Abietinolic, $C_{16}H_{24}O_2$, $46-50\%$.	Pimarolic, $C_{18}H_{28}O_2$, $48-50\%$.	$4-5\%$. Laricinolic, C_{15}-$H_{28}O_2$, $55-60\%$.	Silvinolic, C_{15}-$H_{26}O_2$, $58-60\%$.	Picea-pimar-olic, $C_{25}H_{44}O_2$, $48-50\%$.	3%. Canadinolic, $C_{15}H_{30}O_2$, $48-50\%$.	Palabietinol-lic, $C_{16}H_{24}$-O_2, $53-57$ $\%$. (α & β).	Beljiabie-tinolic, C_{16}-$H_{24}O_2$, $42-50\%$. (α & β).
α-acid, pptd. by alcoholic lead acetate.	($95-96°$) K_1, cold; more with excess.	($90-91°$) K_1, cold or hot.	($80-81°$) K_1, more with ex-cess.	($85-90°$) K_1, I_1.	($90-95°$) K_1, cold and hot.	($89-95°$).		
β-acid, not pptd. by alcoholic lead acetate.	($93-94°$) K_1, cold gradually increasing.		($85-86°$) K_1, more cold, with excess of KOH.	($89-95°$) K_1, I_1.	($88-94°$) K_1, cold and hot I_1.	($90-95°$) K_1.		

COMPOSITION OF CONIFEROUS RESINS (CONTINUED).

	Strassburg	Bordeaux	Venice	Finland	Jura	Canada	Turpentine from	White pitch (Russian "Beljivar")
Indifferent Resins.								
Insoluble in alkalies	Abietoresene, $C_{19}H_{28}O$ (168–169°), 12–16%.	Bordoresene, viscid, 5%.	Resene, indefinite, 14–15%.	Silvoresene (58–60°), 20–21%.	Juroresene, $C_{19}H_{28}O$, 10–12%.	Canadoresene, $C_{19}H_{30}O$ (170°),1–12%.	Paloresene, 10%.	Beljoresene, $C_{21}H_{32}O$, 15–18%.
Essential Oil.								
A. Readily volatile with steam	B. p. 162–163°, 24–25%.	B. p. 150–175°, 14%.	B. p. 155°, 15–16%.	B. p. 155–163°, Sp. gr. .840, 15%.	32–33%.	23–24%. Laevorotatory	B. p. 155–172°, 20–22%. Sp.gr. 0.864 Dex-trorotatory	B. p. 158–165° dex-trorotatory, 20 to 30%. Sp.gr. 0.863. Sol. in 90% alcohol,1:10. Traces.
B. Tailings	4–6%.	15%.	B. p. 190°, 5–6%.					
Minor Constituents.								
Bitter principle, alkaloid, succinic acid, colouring matter, water, and impurities.	1–2%.	2–4%.	1–2%.	1–2%.	1–2%.	1–2%.		
Reference.								
Original	Arch. Pharm., 1900, p. 411.	Arch. Pharm., 1900, p. 630.	Arch. Pharm., 1900, p. 387.	Arch. Pharm., 1901, p. 167.	Arch. Pharm., 1900, p. 616.	Arch. Pharm., 1900, p. 489.	Arch. Pharm., 1902, p. 568.	Arch. Pharm., 1902, p. 584.
Abst. Jour. Chem. Soc.	1900. i, 679.	1901. i, 220.	1900, i. 680.	1901, i. 397.	1901, i. 91.	1900. i. 678.	1903, i. 105.	1903. i, 106.

[1] K_1, K_2 indicate in this table the formation of a mono- or di-potassium salt, respectively. I_1 indicates the formation of a monoiodo-derivative.

[2] The oleo-resin of *Picea vulgaris* grown at Siebenbürgen gave very similar results to the Jura specimen, but the formula of picea-pimarinic acid is given as $C_{19}H_{30}O_2$, that of the picea-pimarolic acids as $C_{18}H_{28}O_2$, and that of the resene as $C_{19}H_{30}O$ (*Arch. Pharm.*, 1902, **240**, 272).

General Properties.—Canada balsam is dextrorotatory ($+1°$ to $+4°$), but the essential oil obtained from it is lævorotatory. This balsam has a sp. gr. of about 0.90, and a ref. index of 1.520 at 20°. This high ref. index differentiates Canada balsam from all other turpentines. A grain of starch laid in the balsam remains visible, whereas in the case of the other balsams it becomes indistinct or invisible.

Analytical Data.—The acid number of Canada balsam ranges from 80 to 87 and the ester number from 4 to 10.

Balsam of Copaiba. Copaiva. Capivi.

Occurrence.—Copaiba is an oleo-resin obtained from the trunk of *Copaifera lansdorfii*, and other South American species of *Copaifera*.[1]

The proportions of resin and volatile oil in copaiba are very variable, and hence the viscosity and sp. gr. are far from constant. The medicinal value of the two constituents of the oleo-resin requires further investigation.

Chemical Composition.—The chemistry of copaiba balsam has been recently investigated by A. Tschirch and by E. Keto (*Archiv. Pharm.*, 1901, **239**, 548).

Adulterants.[2]—Balsam of copaiba is liable to sophistication in various ways, though gurjun balsam, oil of turpentine, castor oil, and colophony are the most usual additions. According to Hager, sassafras oil has been employed, but the price of this oil would usually prohibit this addition.[3]

Commercial Varieties and General Properties.—There are several well-defined commercial varieties of copaiba balsam which take their names from the port of exportation.

[1] See Umney and Bennett, *Pharm. Jour.*, 1901, **1**, 324.

[2] A new adulterant of copaiba—segura balsam—a cheaper oleo-resin, has been described by M. Utz (*Pharm. Zentralh.*, **49**, 16). It is a dark brown viscous liquid with a pleasant aromatic odour. Readily soluble in chloroform, benzene, petroleum ether, and carbon tetrachloride; partially in alcohol. When steam distilled, it yields from 30 to 40% of essential oil which has a sp. gr. 0.9451 at 15°.

The oleo-resin gives a reddish-brown colour with sulphuric acid; yellowish-green with nitric acid; red-brown with vanillin and hydrochloric acid; a light brown with stannous chloride, in the cold and on heating. A mixture with Maracaibo balsam causes increase of sp. gr., and the ester value with a lowering of the acid value; the cold saponification value is only slightly affected. It is probable that but little segura balsam is used as the adulterant, but its essential oil, or a mixture of the oil with segura balsam, is employed.

[3] Hager detects oil of sassafras by mixing 1 c.c. of the sample with 2 c.c. of concentrated sulphuric acid; after the mixture has cooled, 20 c.c. of alcohol are added, the mixture heated to boiling, and set aside. With pure copaiba a milky-greyish or reddish-yellow liquid is obtained on addition of the alcohol, and on boiling the liquid becomes clear and yellow, and a resinous compound settles to the bottom. If oil of sassafras be present, addition of alcohol produces a dark brown colour, becoming on boiling still darker with a violet tint.

Maracaibo balsam is the only variety of copaiba recognised by the German Pharmacopœia. The essential oil distilled from this balsam is typical copaiba oil having sp. gr. about 0.900 to 0.910, and an optical rotation ranging from —7° to —35°. The residue consists almost entirely of resin acid, namely: *β-meta-copaivic acid*, $C_{10}H_{16}O_2$, crystallising in pointed prisms, m. p. 89 to 90°, and *illuric acid*, $C_{20}H_{28}O_3$, melting at 128°.

Para balsam is very variable in quality, but is remarkable for its fluidity and its high proportion of essential oil. The resin of this balsam contains, besides indifferent *resenes, para-copavic acid*, $C_{20}H_{32}O_3$, crystallising in pointed and quadratic leaflets, m. p. 145 to 148°, and soluble in ammonium carbonate solution; and *homo-para-copaivic acid*, $C_{18}H_{28}O_3$, m. p. 111°, and insoluble in ammonium carbonate, but soluble in sodium carbonate solution.

Maturin balsam is of golden-yellow colour, fairly thick, and is not fluorescent. It has a somewhat more pleasant odour than most varieties of copaiba balsam.

Maranham balsam is a thick, golden-brown liquid, and is most esteemed for the manufacture of capsules.

African (Illurin) balsam is of uncertain botanical origin, though probably derived from a species of *Copaifera*. It is distinguished from other copaibas by yielding a dextrorotatory oil, and its presence in the balsam used in medicine is specially guarded against in the British Pharmacopœia by means of this property. African balsam has a high sp. gr. (0.985 to 1.000), is of fairly thick consistence, exhibits a slight fluorescence, and has a pungent, pepper-like odour. It deposits crystals on standing, and yields about 40% of volatile oil on distillation with steam (see page 85). The acid value of illurin balsam is given as 57 to 60, and the ester number at from 9 to 10. *Illuric acid*, $C_{20}H_{28}O_3$, the chief resin acid of African balsam, forms hexagonal tables, m. p. 128° (Tschirch, *Pharm.Central.*, 1891, 337). It is probably identical with the crystalline acid described by Umney and by Peinemann, and possibly also with Fehling's "*oxy-copaibic acid.*" The essential oil of African copaiba has, according to Parry and Bennett, been extensively used for the adulteration of peppermint oil.

Specific Gravity.— The *sp. gr.* of copaiba balsam varies considerably and only gives reliable indication of the quality of the article when considered in conjunction with the proportion and characters of the volatile oil present. The thinner varieties of balsam containing

a high proportion of oil have a sp. gr. as low as 0.916 (as in the case of Para balsam) whereas the sp. gr. of the thicker varieties often exceeds 0.990, and occasionally reaches 1.000 or even more. The sp. gr. limits are from 0.916 to 0.995, but these figures are sometimes slightly exceeded.

Optical Rotation.—As a rule, the colour of copaiba balsam is too deep to allow of the observation of its *optical rotation*, but the optical activity of the essential oil is an important character.

Essential Oil.—The proportion of this substance present in copaiba balsam is very variable. In cases where the balsam is intended for distillation the amount of oil is important. The percentage of oil in genuine balsams usually ranges between 40 and 75% rarely much exceeding the latter figure. As a rule, the precentage seldom exceeds 60, except in the case of the low-gravity Para copaiba. As much as 92% of oil has been recorded, but such a sample was probably adulterated with turpentine.

Oil of Copaiba.—The estimation of the essential oil present in copaiba is best ascertained from the loss of weight suffered by the sample at about 120°, when, except in rare cases, the residual resin will be hard and friable. The resin should never exceed 60%, and is frequently as low as 35% or even less. For the examination of the characters of the oil, 100 grm. of the balsam should be steam-distilled in the usual way. Generally speaking, the only adulterants which will affect the characters of the oil thus obtained are gurjun balsam and turpentine (unless the admixture of African balsam of copaiba be included[1]). The sp. gr. of the oil from genuine copaiba ranges, according to Schimmel & Co., between 0.900 and 0.910, but these limits are too narrow, as pure samples will often yield an oil of sp. gr. 0.898. The limits 0.895 and 0.910 are safer. The optical rotation of oil of copaiba varies between —7° and —35°.

E. J. Parry (*Chem. and Druggist*, 1907, **71**, 518) states that an enormous amount of adulteration is being practised. African copaiba reduces the optical rotation of the essential oil, although the resin still answers the other British Pharmacopœia tests. He believes that at times genuine samples of Maracaibo balsam fall outside the revised British Pharmacopœia limits, —14° to —17° for 100 mm. for the optical rotation of the essential oil, but suggests that in the majority

[1] In the presence of African copaiba, the oil obtained by steam distillation will exhibit comparatively feeble lævorotation, or if the proportion be very large, the oil may be dextro-rotatory.

of cases the low rotation is due to some adulterant, probably African copaiba.

In the *Year-book of Pharmacy*, 1908, 59 results obtained by Evans are given relating to samples of Maranham, Maracaibo, and Carthagena copaiba, which shows that the Maracaibo variety consistently gives lower figures than the Maranham variety. Evans thinks that the suggested lower figure of —7 may exclude genuine samples. G. Weigel (*Chemist and Druggist*, 1907, **71**, 617) distilled 100 samples of oil and found [α]_D ranging from —5 to —28. This author believes that if limits were placed from —5 to —25, 90% of genuine oils would be included.

The oil distilled from pure balsam of copaiba is completely soluble in absolute alcohol and in 4 times its volume of petroleum spirit.

The following figures by J. C. Umney show the properties of the oil from African balsam as compared with those of the oils yielded by Maracaibo and Para balsams:

	African	Maracaibo	Para
% of volatile oil in balsam	32	42	64.3 to 80.2
Sp. gr. of oil at 15°	0.9180	0.9050	0.9060
Rotation in 200 mm. tube	+20.7°	—34.3°	—28.9°
Solubility in absolute alcohol at 15°	not sol. in 50	1 in 1	1 in 1
Range of b. p.	260° to 273°	245° to 255°	252° to 260°

No other differences of importance were observed by Umney, except that the oil from the African balsam reduced auric chloride in chloroform solution (with 1% of alcohol), while the other oils did not.

Copaiba resin is not now official in the United States Pharmacopœia, According to Umney and Bennett, it is soluble in alcohol, ether, and carbon disulphide, forming acid solutions. 1 grm. should neutralise at least 21.5 c.c. of N/10 alkali when titrated in alcoholic solution with phenolphthaleïn.

Identification and Analytical Data.—The characters ascribed to copaiba by different authorities vary greatly. In the British Pharmacopœia of 1885 the sp. gr. was given as ranging from 0.940 to 0.993, but in the edition of 1898 this was extended from 0.916 to 0.995. The United States Pharmacopœia (8th Rev.) allows a sp. gr. from 0.950 to 0.995 at 25°. The German Pharmacopœia, edition 3, allowed a range from 0.960 to 0.990, but in edition 4 this was re-

stricted to 0.980 to 0.990. These varying requirements are due to the different values attached to the essential oil of copaiba, the British Pharmacopœia requiring a minimum of 40%, whereas the German Pharmacopœia limits the proportion of oil to less than this amount.

The *United States Pharmacopœia* allows 50% of oil in balsam of copaiba. It is further directed that 1 grm. of copaiba, dissolved in 50 c.c. of alcohol, should require not less than 2.3 c.c., and not more than 2.8 c.c. of N/2 alcoholic potassium hydroxide for neutralisation to phenolphthaleïn. The nitric and acetic acids colour test for gurjun balsam is included (using, however, 1 c.c. of glacial acetic acid). 5 c.c. of the balsam, when shaken with 15 c.c. of alcohol and heated to boiling for 1 minute, should yield no oily drops to the solution on allowing it to cool and stand for 1 hour (absence of paraffin oils). Twenty drops of copaiba, when boiled with 1 c.c. of alcoholic potassium hydroxide (10%) solution for 2 minutes and cooled, and twice the volume of ether added, should not cause the production of a gelatinous mass (absence of fixed oils). 1 grm. of copaiba, if shaken with 10 c.c. of ammonia-water (10%), and allowed to stand 24 hours in a closed vessel, will produce a turbid solution, but this should not gelatinise nor should a firm mass be produced (limit of resin).

Umney and Bennett (*Pharm. J.*, 1901, 1, 324) suggest that the official requirements for copaiba balsam should be revised as follows: A more or less viscid liquid, generally transparent and occasionally fluorescent; yellow or brown, having a peculiar aromatic odour, and a persistent acrid, somewhat bitter taste. Sp. gr., 0.975 to 0.995. Entirely soluble in absolute alcohol, and in 4 volumes of petroleum spirit, the latter solution yielding only a slight filmy deposit on standing. It should evolve no odour of turpentine oil when heated, and should not lose more than 45% when heated in a water-bath for 48 hours. 3 volumes should form a transparent mixture when added to 1 measure of ammonium hydroxide (10%). The volatile oil should have a rotation of —7° to —21° for 100 mm., and should not boil under 250° (absence of African balsam). It should give a negative result with the glacial acetic and sulphuric acids test (p. 80, absence of gurgun balsam). A solution of 1 grm. in 50 c.c of absolute alcohol should neutralise at least 13.5 c.c. of N/10 alkali hydroxide on titration with phenolphthaleïn (presence of a sufficient proportion of resin acids).

The same authors have recorded the following characters for 5 specially selected typical samples of copaiba balsam:

	Bahia	Cartagena	Maracaibo	Maranham	Para
Balsam					
Sp. gr.	0.938	0.970	0.969	0.990	0.920
% of oil	49.7	41.3	42.5	41.8	62.4
United States Pharmacopœia ammonia test.	turbid	clear	clear	clear	turbid
Acid number	33.7	56.0	50.2	81.5	33.1
Ester number	15.3	28.0	12.1	12.8	26.9
Resin					
Physical characters	soft	brittle	firm	brittle	very soft
Acid number	73.1	135.7	80.3	136.3	68.9
Ester number	73.0	45.1	49.9	36.7	87.2

The characters of the essential oil from these samples were not distinctive. The sp. gr. ranged from 0.903 to 0.908, and the b. p. from 245° to 275°. The oils were soluble in an equal quantity of absolute alcohol, and their optical rotation for 1 dcm. varied from —7° to —21°. The erroneous statement made in the British Pharmacopœia (1898), that the optical rotation of copaiba oil varies from —28° to —34°, is the result of a careless blunder (see F. W. Short, *Pharm. Jour.*, 1900, **1**, 54). Gildemeister and Hoffmann give the range as from —7° to —35°.

Copaiba resin consisting chiefly of free resin acids, the balsam has a very high acid number, but an insignificant ester number. The following table gives the limits for the analytical results recorded by various observers for the different varieties of balsam of copaiba:

Variety of balsam	Characters of balsam			Essential oil	
	Sp. gr.	Acid number	Ester number	%	Sp. gr.
Angostura	0.980 to 1.009	75 to 85	7 to 20	40 to 45	0.906
Bahia	0.980	34 to 98	5 to 15	40 to 45	0.908
Carthagena	0.950 to 0.965	56 to 88	5 to 28	50 to 55	0.904
Maracaibo	0.980 to 0.998	50 to 98	0 to 15	50 to 65	0.895 to 0.907
Maranham	0.990	81.5	13	42 to 50	0.902
Maturin	0.980 to 0.988	75 to 85	4 to 13	45 to 50	0.898
Para	0.915 to 0.990	25 to 62	2 to 33	40 to 90	0.898 to 0.904
Surinam	0.907 to 0.961	15 to 59	10 to 18	41 to 72	0.910
African (illurin)	0.985 to 1.00	57 to 60	9 to 10	40	0.918
Gurjun balsam	0.955 to 0.980	5.8 to 20	1 to 10	55 to 82	0.915 to 0.930

The wide variations recorded above are probably due to certain of the samples being adulterated.

L. F. Kebler (*Amer. J. Pharm.*, 1897, **69**, 577) has published the results of the examination of various samples of commercial copaiba, as have also E. W. Bell (*Pharm. J.*, 1900, **67**, 99) and E. W. Mann

(*Pharm. J.*, 1903, **70,** 419). The last-named found that the greater
number of the commercial samples examined by him responded to
the colour tests for gurjun oil, although in other respects they conform
to the description of a genuine sample.

Detection of Adulterants.—*a.* **Gurjun balsam** is the product of
several species of Dipterocarpus, and presents a close general re-
semblance to copaiba. It is said to contain a crystalline substance
known as *gurjunol*, $C_{20}H_{28}(OH)_2$, m. p. 126° to 129°, while, according
to Tschirch and Weil, a neutral resene, containing $C_{17}H_{28}O_2$, is present.
The sp. gr. of gurjun balsam averages about 0.964, while that of the
essential oil (which is sometimes present to the extent of 80 to 82%)
ranges from 0.915 to 0.930, and hence in its presence the sp. gr. of
copaiba oil will be slightly raised. Gurjun oil is usually strongly
lævorotatory (—55° to —130°), but several specimens of dextrorota-
tory oil have been met with. As a rule, however, the lævorotation
of copaiba oil will be considerably increased by an admixture of
gurjun oil. Gurjun oil distils almost completely between 255° and
265°, the main constituent being a sesquiterpene boiling at 255° to
256°, at which temperature a large fraction of the oil passes over.

Copaiba balsam adulterated with gurjun balsam is not quite clear,
and frequently exhibits prisms of gurjunic acid under the microscope.
According to E. Hirschsohn, gurjun balsam is incompletely soluble
in ether, whereas copaiba balsam gives a clear solution. Alcoholic
lead acetate solution gives a cloudiness with an alcoholic solution of
copaiba, which disappears on warming, while with gurjun balsam no
reaction takes place.

L. B. Kebler (*Amer. J. Pharm.*, 1895, **67,** 394) considers that no
dependence can be placed on the physical characters of the sample.
He considers that the ammonia test is misleading, the acid number
unreliable, and Hager's colour test unsatisfactory, especially if the pro-
portion of gurjun balsam be less than 25%. The most reliable colour
test for the identification of gurjun balsam is the "Turner reaction"
(*Amer. J. Pharm.*, 1908, **80,** 14): 3 to 4 drops of balsam are dissolved
in 3 c.c. of glacial acetic acid and the mixture is carefully poured on to
the surface of 2 c.c. of concentrated sulphuric acid contained in a small
test-tube. When pure copaiba balsam is present, the acetic acid solu-
tion remains colourless or assumes a pale yellow tint, whereas in the
presence of Gurjun balsam a dark violet coloration of the acetic acid
solution is produced. Turner states that 5% of Gurjun balsam can

be detected by this means, but Utz (*Chem. Rev. Fett-Harz-Ind.*, 1908, **15,** 220), by collecting and testing the oil fraction b. p. above 200°, was able to identify 2%. The colour test may always be applied with advantage to the distilled oils, since certain fish oils give evanescent colours, and these oils are not of course found in the distillate. Oil of valerian is also said to give a similar coloration.

b. **Oil of turpentine** may be readily detected in copaiba balsam by steam-distilling the sample, the volatile oil of the balsam and the oil of turpentine passing over. The latter distils before the copaiba oil, oil of turpentine, boiling at about 160°, and oil of copaiba at 240° to 250°. The odour of the turpentine can be detected when the first few drops of distillate are heated on a watch-glass, by which means 2% or 3% of the adulterant may be detected. An idea of the amount of oil of turpentine present may be obtained by observing the sp. gr. and b. p. of the distilled oil. The presence of oil of turpentine in copaiba balsam reduces the sp. gr. and lowers the acid and ester numbers, while it increases the % of essential oil, which has a lower sp. gr. and opt. rot. than genuine oil of copaiba.

c. **Fatty Oils.**—The presence of fatty oils in copaiba balsam renders the separated resin soft, and reduces the % of essential oil in the sample. The sp. gr. and acid mumber of the sample are also lowered, while the ester number is raised.

According to Utz (Schimmel & Co. Report, April, 1906, 13) commercial samples of copaiba balsam in Abbe's refractometer show a ref. index varying from 1.5088 to 1.5288. Gurjun balsam gives similar values, but the presence of fatty oils or turpentine lowers these figures considerably.

For the detection of *castor oil* in copaiba balsam L. Maupy (*Jour. Pharm. Chim.*, 1894, 362) recommends the following method, based on the fact that castor oil yields *sebacic acid* and *caprylic alcohol* on dry distillation with excess of potassium hydroxide: 10 grm. of the sample are heated with dry potassium hydroxide in a silver dish. The mass is stirred and heated until all the volatile oily matters are driven off. In the presence of castor oil, the odour of caprylic alcohol will be noticeable. On cooling and thoroughly separating the upper resinous layer, the lower white liquid portion is treated with 50 c.c. of water, boiled and filtered. Sebacic acid separates out on cooling if the sample contained castor oil. The acid may be further identified by converting it into the lead salt.

For the determination of *fatty oils*, J. Muter (*Analyst*, 1876, **1**, 160) recommends a process based on the insolubility of oleate and ricinoleate of sodium in ether-alcohol, and the solubility of the sodium salts or copaiba resin acids in the same solvent.

d. **Colophony.**—L. E. Walbum (*Pharm. Zentrh.*, 1907, **48**, 437), has given the following method for the detection of colophony in copaiba balsam: 4 c.c. of a 1% solution of ammonia and 1 c.c. of acetone are mixed; to this solution 2 grm. of the balsam dissolved in 6 grm. of ether are added. The whole is well shaken, then allowed to stand until the lower aqueous layer is clear. In the presence of colophony this layer will be darker in colour than a solution containing 2 grm. of balsam in 5 c.c. of absolute alcohol prepared for the purpose of comparison. This colour reaction is only produced by colophony; Canada balsam, mastic, dammar, sandarac, etc., mixed with copaiba balsam give no such colour under similar conditions. This test will readily detect 2% of colophony and even 0.5% will give a definite indication.

Cativo, from *Prioria copaifera*, presents no similarity to copaiba balsam, although it has been supposed to resemble it. (See E. M. Holmes; J. C. Umney; *Pharm. J.*, 1902, **69**, 296.)

GUM-RESINS.

The gum-resins constitute a group of natural products which occur as exudations from various plants. These products consist of a mixture of gums with various resins, a small percentage of essential oil, and traces of colouring and undefined matters.

The gum-resins occur in commerce either in tears or masses. The tears are the purer form, as they usually consist of the pure exudation, whereas the latter variety is liable to accidental admixtures, such as woody fibre, etc., besides intentional adulterations of a varied kind. Stones, sand, gypsum, etc., are among the mineral sophistications met with, and adulteration with colophony and other low-priced resinous matters is also practised.

When the natural gum-resins are treated with water, gum, sugar and other carbohydrates are dissolved, but the extraction is apt to be imperfect owing to the protective action exerted by the resinous constituents. A better method of proximate analysis is to treat the substance with alcohol of 95% strength, which dissolves the resinous matters, leaving the carbohydrates practically intact, and these can

then be readily extracted with water, any woody fibre or added mineral matters being left as a residue. •

Mauch's method (page 8) is well suited for the resolution of gum-resins.

AMMONIACUM.

This gum-resin is the product of *Dorema ammoniacum*, one of the *Umbelliferæ*.[1] It occurs in commerce in tears, and in masses of ag-glutinated tears, which are apt to contain extraneous matters. At ordinary temperatures ammoniacum is hard and brittle, but softens by the heat of the hand. It has a faint, somewhat unpleasant odour, which is accentuated on warming.

A specimen of ammoniacum examined by Tschirch, Luz, and Osterle contained 3.5% of matter insoluble in alcohol and water, in addition to the salicylic ester of *ammoresinotannol*, $C_{18}H_{29}O_2.OH$; traces of free salicylic acid; volatile acids, such as acetic and caproic acids; and about 0.5% of essential oil. No sulphur or umbelliferone could be detected.

The following analyses of apparently authentic samples of ammoni-acum have been recorded:

Number	Ethereal oil, %	Water, %	Ash, %	Gum, %	Resin, %	Observer
1	1.27	5.10	2.00	26.10	65.53	Plugge
2	....	....	....	22.4	72.0	Buchholz
3	....	....	....	18.4	68.6	Bracounot
4	....	....	....	19.3	....	Moss
5	1.43 to 6.68	0.81 to 3.27	2.02 to 3.27	......	47.2 to 69.2	Hirschsohn

According to some authorities, a small quantity of gelatinous matter and sugar are also present.

By dissolving ammoniacum in a 60% aqueous solution of chloral hydrate and pouring the solution into strong alcohol, Mauch obtained 21% of pure gum. •

Identification and Analytical Data.—5 grm. of finely powdered material are boiled for 15 minutes with about 13 c.c. of fuming hydro-chloric acid and filtered. The result in clear filtrate on being care-

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[1] The so-called African ammoniacum is obtained from *Ferula tingitana*, and differs from the ordinary or Persian product in containing *umbelliferone* (compare Galbanum, page 97).

fully supersaturated by adding ammonia water should display no blue fluorescence with reflected light. •

The turbid liquid obtained by boiling 1 part of ammoniacum with 10 parts of water produces a dirty reddish-violet colour with ferric chloride solution (Tschirch). The ignited ammoniacum should not leave more than ˙5% of ash. Dieterich states 10%. These tests easily differentiate this resin from galbanum.

The following analytical limits and characters of varieties of ammoniacum have been recorded:

	A. Kremel		E. Dieterich		Beckurts and Brüche	
	Persian	African	Crude Persian	Purified Persian	Purified Persian	Persian in tears
Sp. gr.........	....	......	....	....	1.19 to 1.21	1.20
Ash, %.......	....	......	....	....	0.79 to 4.47	3.84
Resin soluble in 96% alcohol.	....	......	46 to 88	66 to 76	59 to 68	56
Acid number (of resin).	100 to 112	59	57 to 105	79 to 135	69 to 80	70
Ester number (of resin)	30.6 to 50.5	123	64 to 91	73 to 98	19 to 38	35

According to Gregor and Bamberger, the methoxyl number of ammoniacum ranges from 8.6 to 11.0.

Asafœtida.

Occurrence.—This gum-resin is the product of several species of *Ferula*, probably chiefly of *F. scorodosmo, F. narthex*, and, according to the British Pharmacopœia, *F. fœtida*. Asafœtida is largely imported from Bombay, to which place it is brought by the gatherers from Persia.

Asafœtida is extensively used in America in the treatment of a disease of horses known as "heaves." The gum-resin is also employed in small quantity as a flavouring agent, in sauces, etc.

Chemical Constituents.—According to Tschirch, the chief constituent of asafœtida is the *ferulic ester* of the alcohol *asaresinotannol*, $C_{24}H_{34}O_5$. This ester forms about 60% of the resin, besides which there are present traces of the free alcohol and free ferulic acid; 25% of gum; traces of vanillin; and up to 7% of an essential oil of complex nature.

General Properties.—Asafœtida occurs in tears separated or sticking together, but more often in large masses having a characteristic odour and taste. Externally it is either yellowish, violet, or brownish. The fresh fracture shows a white colour which changes gradually to a pink or violet and finally to a light yellowish-brown.

The British Pharmacopœia of 1885 described asafœtida as occurring "rarely in tears; usually in irregular masses," but in face of this fact the edition of 1898 describes asafœtida as occurring "in rounded or flattened tears." Tears of asafœtida are so scarce that were the consumers (chiefly veterinary surgeons) restricted to this form, the supply would be insufficient. The tears are much purer than asafœtida in mass, which is contaminated with much dirt and woody fibre.

Commercial asafœtida is sometimes adulterated with cheaper resins, such as colophony, but the most common impurity is an abnormal proportion of mineral matter. The British and United States Pharmacopœias require that asafœtida should not yield more than 10% of ash, while the German Pharmacopœia fixes 6%, and the Dutch Pharmacopœia 20% as the ash limit. Mörner and Fristedt examined a sample of asafœtida in tears, which contained 86% of mineral matter, consisting chiefly of calcium sulphate. J. Muter has also described samples of asafœtida containing as much as 70% of stones. These no doubt had their origin in the practice, formerly much in vogue in the East, of packing drugs with as many heavy fragments of stone as could be got into the bale or cask.

Analytical Data.—In addition to an ash-limit of 10%, the British Pharmacopœia further requires that asafœtida shall contain not less than 65% of matter soluble in alcohol of 90% strength. The United States and German Pharmacopœias requires only 50% of soluble matter under these conditions. It is held by most authorities that the British Pharmacopœia requirements of ash and matter soluble in alcohol are unpractical and far too stringent, and that an ash limit of 20% and an alcohol solubility of not more than 50% would be preferable.

Since by far the greater proportion of commercial asafœtida contains considerably more than 10% of mineral matter, in order to obtain specimens of British Pharmacopœia quality either fine tears must be used, or the purified resin from which the mineral matter has been removed must be employed.

The ash yielded by asafœtida does not afford an accurate criterion of the mineral matter of the sample, as the sulphur present exists, to a

great extent, in organic combination and is fixed by the bases; while a
portion of the sulphate is liable to be reduced during ignition by the
organic matter. Hence Mauch treats the sample with ten to fifteen
times its weight of 60% chloral hydrate solution in water,[1] when the
gum and resin slowly dissolve. The residue is washed on to an ashless
filter-paper with chloral hydrate solution and then washed with alcohol,
and after drying the residue is ignited and weighed.

W. A. Buckner (*Year-book Pharm.*, 1891, 211) found 5 samples
of asafœtida to contain from 27 to 45% of their weight of matter
soluble in 90% alcohol, while one other sample contained 59.5% of
alcohol-soluble matter. The ash of the five samples ranged from
19.45 to 56.03%, the portion insoluble in hydrochloric acid varying
from 1.37 to 21.96%.

From an examination of 11 samples of asafœtida, Martin and
Moor (*Analyst*, **25**, 1900, 2) found the ash to range from 26.4 to
63.1%, and the ash insoluble in hydrochloric acid to range from 42 to
84% of the total, while in one case the ash dissolved readily in hydro-
chloric acid with much effervescence, leaving only 3.6% insoluble.
The proportion of the sample soluble in 90% alcohol ranged from
14.8 to 39.8% in twelve samples. (Similar figures have also been
published by R. W. Moore, *J. Soc. Chem. Ind.*, 1899, **18**, 987; M. I.
Wilbert, *Amer. J. Pharm.*, 1901, **73**, 131; and others.)

According to Hirschsohn, good samples of asafœtida should yield
not less than 11% of soluble matter to petroleum ether when the
residue is dried at 17°, and not less than 6% of this residue should
be lost on being heated to 120°. The use of these arbitrary tempera-
tures is rendered necessary by the occurrence of volatile soluble con-
stituents in asafœtida. 11 samples of the gum-resin were found by
Hirschsohn to give the following results by treatment with petroleum
ether:

> Extract, dried at   17° ....from 1.50 to 13.45%.
> Extract, dried at 120° ....from 1.01 to 4.65%.

The following table gives the acid and ester numbers of asafœtida
according to several observers. The figures refer to the *extracted
gum-resin*, with the exception of those obtained by K. Dieterich, which
lose their meaning unless the ash is known:

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[1] Whether by a "60% solution" is meant a mixture of 60 parts of chloral hydrate with
40 of water, or a solution of 60 grm. of chloral hydrate in 100 c.c. of water is uncertain.

Character of sample	Acid number	Ester number	Observers
Extracted gum-resins............	27 to 55	145 to 182	A. Kremel
Extracted gum-resins............	11 to 82	82 to 129	E. Dieterich
Extracted gum-resins....	27 to 45	181 to 214	Beckurts and Bruche
Commercial samples............	65 to 80	80 to 130	K. Dieterich

According to Gregor and Bamberger, the ·methoxyl number of asafœtida ranges from 7 to 18.

Tincture of asafœtida, B. P., is prepared by extracting 200 grm. of the gum-resin with 1 litre of 70% alcohol. The solubility of asafœtida in alcohol of this strength is sometimes more and sometimes less than its solubility in 90% alcohol, and since the gum-resin, as usually met with, rarely comes up to•the pharmacopœial standard of alcohol-solubility, and resulting tincture will practically never contain the calculated standard of solid matter in solution. Thus, if 65% (the pharmacopœial standard) of asafœtida were soluble in 70% alcohol, the tincture should contain 13.0 grm. of extract per 100 c.c. Martin and Moor, however (*Analyst*, **25,** 3), found that the total solids from 7 samples of the tincture ranged from 4.3 to 8.5 grm. per 100 c.c. Tincture of asafœtida is therefore always much below its presumed strength, and the minimum amount of extract the tincture should contain should be specified. J. C. Umney (*Pharm. J.*, 1902, **69,** 492) considers 10 grm. of solids per 100 c.c. of tincture to be a reasonable standard. The sp. gr. of tincture of asafœtida ranges from 0.910 to 0.915.

Oil of asafœtida is a liquid of disgusting odour, having a sp. gr. of about 0.975 to 0.990 and an optical rotation of about $-10°$ in a 100 mm. tube. The oil was examined by Hlasiwetz in 1849, who stated that it was composed of *hexenyl sulphide*, $(C_6H_{11})_2S$, and hexenyl disulphide, $(C_6H_{11})_2S_2$, and was devoid of any oxygen or nitrogen. According to Brannt, asafœtida oil contains allyl sulphide and disulphide. Semmler, however, denies the accuracy of these results, and found the oil to contain pinene; a sesquiterpene having an odour resembling lavender; sulphur compounds having the composition $C_7H_{14}S_2$ (about 45%), $C_{10}H_{20}S_2$ (the constituent to which the oil owes its odour, about 20%), $C_8H_{16}S_2$, and $C_{10}H_{18}S_2$; and an oxygenated compound having the formula $(C_{10}H_{16}O)_n$, present to the extent of about 20%. This substance, by treatment with sodium, yields cadinene.

Elemi.

Occurrence.—The chief elemi resin of commerce is that from Manila, and is the product of *Canarium commune*. Several of the *Burseraceœ*, however, contribute to the resin as generally known.

Chemical Composition.—The chemistry of Manila elemi has been investigated by Tschirch and Cremer (*Arch. Pharm.*, 1902, **240,** 293). The leading constituents appear to be a mixture of two crystalline resins, α- and β-amyrin, $C_{30}H_{49}OH$; α- and β-elemic *acids*, $C_{37}H_{56}O_4$ and $C_{44}H_{80}O_4$; an amorphous *resene*, $C_{15}H_{30}O$; and *bryoidin*, $C_{21}H_{42}O_3$, together with an essential oil consisting of dextro-phellandrene and dipentene. Carana elemi (from *Protium carana*) and Colophonia elemi (Mauritius) have also been investigated by Tschirch and Saal (*Arch. Pharm.*, 1903, **241,** 149), and Caricari elemi (Brazilian) by Tschirch and Reutter (*Arch. Pharm.*, 1904, **242,** 117). All these varieties contain the two isomeric amyrins.

Uses.—Elemi is employed for special purposes in lithographic work, and it is also used to some extent in the varnish industry.

Adulterants.—This gum resin is often sophisticated with common turpentine and colophonium.

General Properties.—When fresh, elemi is a clear pale liquid consisting of resins dissolved in essential oil with a small amount of crystallised resins in suspension. On keeping it changes to a soft crystalline yellow resin and sometimes becomes quite hard. All the elemis are softer than colophony, and can easily be cut with a knife. They have an odour like turpentine, and in addition a smell resembling aniseed, cloves, or lemon, according to the variety.

Analytical Data.—Dieterich has found for the soft Manila elemis the following analytical figures:

Acid value, 17.8 to 24.5.

Ester value, 6.1 to 25.5.

Saponification value, 25 to 50.

Colophony and common turpentine when added increase the acid and saponification values.

Detection of Adulterants.—Two tests have been put forward by P. Stoepel (*Apoth. Ztg.*, 1908, **23,** 440) for the detection of elemi and the identification of ordinary turpentine as an adulterant. When heated on a water-bath, elemi melts to a clear yellowish-green liquid, which is coloured eosin-red when dilute sulphuric acid (1:4) is added.

Pure elemi when dissolved in absolute alcohol reacts neutral to blue litmus-paper, whereas when common turpentine is present the blue colour changes to red. When water is added to this alcoholic solution a pure white milky emulsion is obtained in the presence of pure elemi, whereas when turpentine is present a resinous brownish yellow flocky precipitate is thrown down.

Galbanum.

Occurrence.—This gum-resin is the product of *Peucedanum (Ferula) galbanifluum* and allied species of the *Umbelliferæ*.

Chemical Composition.—Galbanum usually contains about 9% of essential oil,[1] but the exceptional proportion of 22% has been recorded. In addition to essential oil, galbanum contains about 27% of gum and impurities, and about 64% of alcohol-soluble resin. This contains traces of free *umbelliferone* with about 20% of umbelliferone present as an ester of *galbaniresinotannol*, $C_{18}H_{29}O_2.OH$, a compound isomeric with the resin-alcohol of ammoniacum.

General Properties.—Galbanum is met with in grains either loose or adhering *inter se* into a mass of a brown-yellow or often faintly green colour, and when fractured appears yellow to yellowish-white.

Identification and Analytical Data.—If finely powdered galbanum be boiled for a quarter of an hour with fuming nitric acid, filtered through a previously moistened filter-paper, and the clear filtrate be carefully oversaturated with ammonia water, the resulting solution when seen by reflected light shows a blue fluorescence. When extracted with 95% alcohol not more than 50% of residue should be obtained.

The following table shows the analytical characters of galbanum as recorded by various observers:

	A. Kremel	E. Dieterich		Beckurts and Brüche	
		Crude resin	Purified	Crude resin	Purified
Sp. gr.	....	....	....	1.109 to 1.133	
Ash, %	....	....	0.1 to 2.1	4.0 to 8.7	
Loss at 100°, %	....	0.4 to 31.3	8.6	....	
Solubility in 96% alcohol = resin, %	74.3; 74.2	1.1 to 31.0	45.6 to 92.2	54 to 63	
		17.8 to 71.5			
On the extracted resin. { Acid No.	28.3; 28.3	5.2 to 68.8	19.3 to 46.3	....	19 to 40
{ Ester No.	119.3; 132.2	82.1 to 179.0	55.7 to 91.4	....	63 to 91

[1] *Oil of galbanum* was included in the 1589 edition of the *Dispensatorium Noricum* and in the *Pharmacopœia Augustana* of 1580. It is a yellow oil of sp. gr. 0.910 to 0.940, and has an optical rotation of + 20° to − 10°. According to Hirschsohn, Persian galbanum yields a dextrorotatory, and the Levant gum-resin a lævorotatory oil. The constituents of the oil include pinene and cadinene.

Myrrh and Bdellium.

Occurrence.—These closely allied substances are the oleo-resinous exudations from the stem of various species of *Balsamodendron* or *Commiphora*.

Commercial Varieties.—At least two distinct varieties of myrrh occur in commerce besides several of bdellium. There is considerable confusion concerning the species of plants which yield true or *Herabol myrrh*, as distinguished from *Bisabol myrrh* and from *bdellium*.[1]

Myrrh formerly came chiefly from Turkey, but now is collected principally in India, Arabia, and Somaliland.

As imported into the United Kingdom, myrrh consists of a mixture of true or Herabol myrrh with several allied products obtained from ' trees of the same genus (*Commiphora* or *Balsamodendron*). These admixtures are picked out on arrival, so that the "gum myrrh elect" is free from them. The chief gum-resins imported in admixture with Herabol myrrh are opaque bdellium, African and Indian bdelliums, and Bisabol myrrh or opopanax, used for the production of oil of opopanax.

Herabol myrrh is the only kind of myrrh officially recognised in pharmacy. If is stated to contain from 50 to 60% of a *gum* of the formula $C_6H_{10}O_5$; 2 dibasic *resin acids* containing, respectively, $C_{13}H_{16}O_8$ and $C_{26}H_{32}O_9$; and *herabol-resene* $C_{26}H_{34}O_5$, which, according to O. Kohler, contains 3 hydroxyl groups, though this statement is disputed by Tschirch. Tschirch and Bergmann have given empirical formulæ for various compounds they claim to have isolated from herabol myrrh, but the chemistry of the subject is in a very confused state.

Bisabol myrrh is largely used in China for the manufacture of joss-sticks. In appearance it closely resembles true myrrh, and acquires the taste of the latter when the two are packed together. The taste of Bisabol is, however, very different, and if used in making *Mist.ferri comp.* it gives the preparation a bitter taste. According to Tucholka, Bisabol myrrh contains 2 *resin acids*, to one of which he assigns the formula $C_9H_{13}O_2$; a neutral *resin* of ketonic character, $C_{20}H_{32}O_4$; and *bisabol-resene*, $C_{29}H_{27}O_6$.

General Properties.—When fresh, myrrh is pale in colour and soft, owing to the presence of a small % of essential oil. It is found

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[1] The botany of the species yielding myrrh and bdellium has been exhaustively described by E. M. Holmes, *Pharm. Journ.*, 1898, **19**, 547; 1899, pp. 26, 77.

in commerce in yellowish, reddish, or brown, granular or irregular masses; internally often marked here and there with whitish veins; translucent when broken in small pieces, having an aromatic odour and a bitter acrid taste.

Identification and Analytical Data.—On treating true myrrh with nitric acid a violet colouration is produced. On this reaction various tests for myrrh have been based, some of which (including that of the British Pharmacopœia of 1898) afford remarkable examples of badly devised and unsatisfactory applications. The subject has been investigated by H. G. Greenish (*Pharm. J.*, 1901, **67**, 666), who finds that the violet colour is yielded in the greatest intensity and purity by adding nitric acid to the ethereal or petroleum-spirit extract of the myrrh.[1]

The method of applying the test recommended by Greenish is to treat 0.5 grm. of the coarsely powdered sample of myrrh with 10 c.c. of ether, and shake at intervals during 10 minutes. 2 c.c. of the filtered liquid is evaporated at a gentle heat, and the capsule containing the residue inverted over another containing strong nitric acid, so that the residue may be exposed to the acid fumes. When thus treated, the residue from Herabol myrrh gradually acquires a violet colour.

Experiments made by A. R. Tankard, in Allen's laboratory, generally confirmed Greenish's observations. The residue obtained on evaporating an alcoholic solution (British Pharmacopœia tincture) of myrrh gave the violet colouration very imperfectly; but by diluting the tincture with water and agitating the liquid with petroleum spirit, the substances to which the reaction was due passed into the latter,[1] and on separating and evaporating the petroleum spirit, the residue gave the reaction very distinctly. Tankard prefers to moisten the residue with nitric acid (sp. gr. 1.42) instead of exposing it to the vapour of the acid. Bromine vapour and bromine water, which have been recommended, give the coloration much less distinctly. 3 samples of *Bisabol* myrrh examined by Greenish gave no violet colouration with nitric acid, but readily responded to Tucholka's test for *Bisabol*. *Bdellium*, *hotai*, and other allied gum-resins gave Greenish a negative result with the nitric acid test.

Old myrrh gives the nitric acid indication far less distinctly than

[1] Greenish found the essential oil obtained by steam distillation of myrrh to give the reaction with great intensity, but the residue left in the distillation flask also gave the reaction, though he considered it possible that this might have been due to the incomplete volatilisation of the essential oil, since the fixed residue retained the odour of myrrh (and gave the violet coloration) after being kept for several weeks "on the top of the air-oven."

fresh specimens, probably owing to volatilisation of the essential oil and oxidation of the resinous matters. In any case, the test only serves for the recognition of *Herabol* myrrh in presence of *Bisabol*, *bdellium*, etc., and it is of no service for the detection of the latter gum-resins in admixture with true myrrh.

According to Tucholka (*Year-book Pharm.*, 1898, p. 180), a direct test for *Bisabol* myrrh consists in treating 6 drops of the solution of the sample in not less than 15 parts of petroleum ether with 3 c.c. of glacial acetic acid, and then cautiously adding without agitation 3 c.c. of strong sulphuric acid. In the presence of *Bisabol* myrrh, a rose-red coloration is produced at the junction of the 2 strata, and the whole of the acetic acid layer shortly acquires a red colour which persists for some time. When *Herabol* myrrh is similarly treated only a slight rose colouration is communicated to the acid layer, and this does not increase, while the contact-line is first green, which changes to brown with a greenish fluorescence. The essential oil from *Bisabol* myrrh gives the rose-red colour reaction very distinctly.

Good samples of myrrh should contain not less than 30% of alcohol-soluble resin, and should leave not more than 8% of ash on ignition (many samples give not more than 4 to 5%). According to K. Dieterich, Herabol myrrh may yield as much as 50% to alcohol, whereas the proportion of resin in Bisabol myrrh is much smaller (sometimes 20%). E. Dieterich states the proportion of myrrh soluble in 96% alcohol at 23%, and the water-soluble constituents at 37 to 52%. These figures probably refer to Bisabol myrrh.

Tucholka found a sample of *Bisabol myrrh* to contain: gum soluble in water, 22.1; gum soluble in soda solution, 29.85; resin, 21.5; bitter principle, 1.5; ethereal oil, 7.8; water, 3.17; and inorganic and insoluble vegetable matters, 13.4%.

According to Flückiger, pure samples of *bdellium* contain about 70% of resin, 30% of gum, and traces of essential oil. The constituents of bdellium resin are not understood, but are probably closely allied to those of myrrh. African and Indian bdellium are sometimes employed in varnish-making.

Hirschsohn states that myrrh should not contain more than 6% of matter soluble in petroleum ether, any larger amount indicating adulteration.[1] He found the following proportions of matter soluble in petroleum ether in samples of genuine bdellium:

[1] This experience is strangely at variance with that of H. G. Greenish, who found a sample of genuine myrrh (previously mixed with twice its weight of sand) to yield 22.8% to

Origin	Dried at 17°	Dried at 120°
India............	13.37	11.29
India.........;................	16.57	9.87
Africa..........................	36.09	35.61
Africa........................	35.68	34.79
Africa.......................	21.70	20.31

The presence of sulphur in the residue left after treatment of the sample with petroleum ether is said by Hirschsohn to indicate the presence of *bdellium*, but this observation requires confirmation.

The following figures for myrrh and bdellium have been recorded by Kremel. The figures all refer to the resin extracted by alcohol, and not to the original gum-resin.

	Sol. in alcohol, %	Acid number	Ester number	Sapon. number
Myrrh:				
Herabol......................	39.5	64.0	95.0	159.0
Herabol.........	42.0	60.2	116.5	176.7
Herabol	23.9	70.3	145.8	216.1
Indian (? bisabol).............	30.7	42.1	130.8	172.9
Bdellium......................	74.3	28.3	119.3	147.6

The following results were obtained by K. Dieterich on samples first thoroughly triturated with water, and thus the substance employed contained gummy matters, etc., as well as resin. The ester values were found by difference.

Myrrh	Acid number	Ester number	Sapon. number	Soluble in alcohol, %
Herabol myrrh................	25.5	204.1	229.6	20
Bisabol myrrh................	20.1	125.5	145.6	50

petroleum spirit (boiling under 80°), while the residue yielded 3.96, 3.72, and 2.55%, respectively, to carbon disulphide, ether, and alcohol used successively.

For the determination of the gum in myrrh, Mauch dissolves from 1 to 2 grm. of the sample in 15 grm. of a 60% solution of chloral hydrate in water, and precipitates the filtered liquid by adding 100 grm. of strong alcohol. He obtained 75.2% of gum by this method.

Gregor and Bamberger found a methoxyl number of about 13 for genuine myrrh.

Tincture of myrrh, B. P. and U. S. P., is prepared by macerating 200 grm. of coarsely-powdered myrrh with a sufficient quantity of 90% alcohol, allowing the mixture to stand with frequent agitation for 7 days (3 days, United States Pharmacopœia), and making the volume finally up to 1,000 c.c.

The distillation process is not directly available for the determination of the alcohol in tincture of myrrh. A useful method, devised by Allen, is described in Vol. 1, under "Tinctures."

Thorpe and Holmes (*Proc. Chem. Soc.*, 1903, **19**, 13) have described the following distillation method for the estimation of ethyl alcohol in tinctures, essences, etc., containing essential oils and volatile substances such as ether, chloroform, camphor, etc. 25 c.c. of the tincture or other liquid, measured at 15.5° is diluted with water in a separating funnel to about 100 or 150 c.c., and sufficient common salt added to saturate the liquid. 50 to 80 c.c. of petroleum ether (boiling below 60°) is now added, and the mixture shaken vigorously for 5 minutes. After allowing the liquids to stand for half an hour, the lower layer in the separating funnel is drawn off and extracted a second time with petroleum ether, if necessary, after which it is placed in a distilling flask. A single extraction will in most cases be found sufficient. The petroleum-ether extracts are washed successively with 25 c.c. of saturated brine, the washings being added to the main quantity of solution in the distilling flask. The liquid in the flask is neutralised if necessary and is then distilled, the distillate being made up to 100 c.c., and its sp. gr. determined as usual. The results obtained require a small correction, owing to the fact that the alcohol present in the tincture is diluted in the distillate to 4 times its original volume, and the errors of the alcohol tables are thus increased. The mean error of the tables at below 40% proof (for example, 0.972 sp. gr.) may be taken as +0.2% of proof spirit, and hence the percentage of proof spirit found by the above method requires a correction of 0.8%, which amount should be subtracted from the result obtained. The method is said to be accurate and to admit of very general application.

J. F. Liverseege (*Chem. and Druggist*, April 18, 1896) has described an indirect method for the estimation of the alcoholic strength of tincture of myrrh, which he considers preferable to any distillation process.

Great variations in the amounts of solids of tincture of myrrh have been observed (T. Macfarlane, *Canadian Bulletin*, No. 34), which are due to the variable amount of alcohol-soluble matters present in the gum-resin. Myrrh containing 30% of alcohol-soluble matter, of which only about 5% is volatile at 100°, should yield a tincture containing about 5 5 grm. of solids per 100 c.c. (C. G. Moor, *"Suggested Standards for Foods and Drugs,"* page 193).

From the examination of a large number of commercial samples of tincture of myrrh by various observers, the sp. gr. at 15.5° was found to range from 0.848 to 0.856, the grm. of solids per 100 c.c. from 3.0 to 6.1, and the alcoholic strength from 82.7 to 86.8% by weight.

Oil of myrrh was obtained by Tucholka from Somaliland *Bisabol* myrrh by shaking out the alcoholic resin solution with pretroleum spirit, evaporating the solvent, and steam distilling the residue. As thus obtained, oil of myrrh is a pale yellow limpid oil of characteristic odour, having a sp. gr. of 0.8836 at 24°, and b. p. at 220° to 270°. It has an optical rotation of —14.3° in a 100 mm. tube, and is alleged to contain a new terpene, *bisabolene*.

INDIA-RUBBER, RUBBER SUBSTI-
TUTES AND GUTTA-PERCHA.

By E. W. LEWIS, A. C. G. I.

POLYTERPENES. ·

Under this heading are included substances having the same empirical composition as the terpenes, but whose fundamental molecules must be assumed to be multiples of $C_{10}H_{16}$. The only examples of such compounds with which we have to deal are the fundamental hydrocarbons of india-rubber and gutta-percha; these are considered in the following pages.

INDIA-RUBBER.

India-rubber is obtained from the latex of trees, of many species, indigenous to tropical countries, more particularly to South America, Africa, and India. Latterly, certain of these species have been shown to be well adapted for cultivation, and extensive plantations are now in existence in Ceylon, the Malay Peninsula, and other countries.

India-rubber latex is obtained from the trees by making incisions in the bark, and so laying open the *laticiferous vessels*. The latex exudes and is collected in various ways, according to the species, locality, etc. It forms an opaque liquid closely resembling animal milk in appearance, and, under the microscope, is seen to consist of an emulsion of globules, in a watery "serum." The globules consist of a substance which, when the latex is "coagulated" by suitable means, is transformed into india-rubber. Whether this transformation is of a "chemical" or merely of a "physical" nature is still undecided.[1] The average size of the globules is different in different latices; globules of the latex from *Hevea braziliensis* vary in diameter from 0.5μ to 2μ,[2] whereas the average diameter of *Funtumia elastica* globules is only about 0.5μ.[3]

[1] See on this subject, Weber, *Ber.*, 1903, 36, 3108; Eduardoff, *Gummi-Zeit.*, 1909, 23, 809.
[2] Victor Henri, *Compt. rend.*, 1907, 144, 432.
D. Spence (*Ind.-rubber J.*, 1908, 36, 233) gives 0.5μ to 2.5μ.
Adriani (Pickles, Brit. Assoc. Rep., 1906) gives 1/12250 in. as the average diameter.
[3] D. Spence, *loc. cit.*

The sp. gr. of india-rubber latex is usually, but not invariably, below that of water; when freed from rubber the sp. gr. of the serum varies from 1.037 to 1.040. The rubber is accompanied in the latex by resins and by a number of other soluble and insoluble impurities.

Analysis of India-rubber Latex.—For the analysis of a rubber latex the following method may be adopted:[1] 100 grm. of the latex are coagulated, by means suited to the particular latex, and the rubber obtained is worked into the form of a thin sheet, and thoroughly digested with water, in order to remove soluble carbohydrates, organic acids, and inorganic salts. These soluble products may be estimated, if desired, by the method of dialysis, described by Spence (*loc. cit.*). The washed rubber is then dried *in vacuo* until constant in weight. The dry rubber is cut up fine, and 5 grm. are extracted with acetone, at the b. p. of the latter; the amount of extract (resins and oils) is determined by direct weighing. The extracted rubber is dried *in vacuo*, and 1.5 grm. is then dissolved in chloroform in the cold. When homogeneous, the solution is heated to the b. p., centrifugalised to separate the mechanical impurities,[2] filtered through a weighed filter of glass wool, covered with muslin, and the residue on the filter washed with chloroform, dried and weighed. The filtrate is evaporated to dryness in a weighed flask, dried in a rapid current of carbon dioxide, then over sulphuric acid until constant in weight. *Nitrogen* is estimated in 20 c.c. of the original latex by Kjeldahl's method, and the *mineral constituents* (ash) by incinerating 20 c.c. of the latex. The results of the analysis may be expressed as in the following example, which represents a (somewhat abnormal) sample of *Funtumia elastica* latex.[3]

Girard and Lindet have recorded analyses of a number of india-rubber latices.[4] In these instances the rubber was estimated by

Water..	76.2%
India-rubber......................................	19.85%
Resins, etc. (soluble in acetone)....................	2.00%
Organic crystalloids (sugars, organic acids, and certain nitrogenous compounds)........................	1.39%
Insoluble impurities (protein, etc.)...............	0.36%
Total nitrogen....................................	0.438%
(Total nitrogen calcd. as protein..................	2.73%)
Mineral matter (ash), chiefly K, Fe, Ca, Mg as phosphate, sulphate, and oxalate largely.............	0.266%

[1] D. Spence, *J. Inst. Comm. Research in Tropics*, 1907, **2**, 115.
[2] Ditmar, *Gummi-Zeit.*, 1906, **20**, 364.
[3] D. Spence, *J. Inst. Comm. Research in Tropics*, 1907, **2**, 115; also 1907, **2**, 45 and 106.
[4] *Bull. Soc. Chim.*, 1898, **19**, 812–815.

adding gradually an equal volume of 95% alcohol to the latex and stirring constantly, when the whole of the rubber collected on the surface of an amber-coloured mother-liquor.

Source of latex	Sp. gr.	India-rubber, %
Pernambuco (*Hancornia*)	0.990	31.6
Africa (probably a *Liana* latex)	0.987	33.4
Parà (*Siphonia elastica*)	0.986	42.6
Nicaragua (*Castilloa elastica*)	0.980	32.3
Algiers (*Ficus macrophylla*)	1.000	37.5
Algiers (*Ficus macrophylla*)	1.005	37.1
Algiers (*Ficus elastica*)	1.001	17.3
Algiers (*Ficus nitida*)	0.971	31.3
Algiers (*Ficus levigata*)	1.005	28.0
New California (*Kickxia africana*)	1.005	27.0

A modern source of rubber not included among the latex-yielding species referred to above is the Guayule shrub, *Parthenium argenta-tum*, A. Gray, the source of the so-called Guayule rubber. This shrub, which is indigenous to Mexico, is cut down and the rubber is obtained from it by various chemical and mechanical processes.[1]

India-rubber.—The crude india-rubber of commerce is of very variable composition. In addition to its fundamental constituent, the actual rubber hydrocarbon, it contains various impurities, some derived from the latex itself, others from extraneous sources. These impurities consist of resins, carbohydrates (including inositol), protein, colouring matters, tannins, mineral compounds and water, which come under the first heading, and such "mechanical" impurities as bark, leaves, sand, clay, stones, etc., which belong to the second class. Plantation rubbers are, as a rule, practically free from impurities of the second class, and in many cases also from water and soluble impurities.[2]

The essential constituent of crude india-rubber is the actual rubber substance, a hydrocarbon, having the molecular formula $(C_{10}H_{16})$. The name "polyprene" was formerly given to this hydrocarbon by Weber,[3] on the assumption that it was a polymeride of isoprene C_5H_8. More recent work by Harries,[4] however, has led to the conclusion that

[1] See *Gummi-Zeit.*, 1908, **23**, 93–94.
[2] Moreover, by carefully controlled coagulation it is possible to reduce the amount of resinous impurity to a minimum. (Cf. Sandmann, *Tropenpflanzer*, 1910, **14**, 180–206.)
[3] See Chemistry of India-rubber, London, 1902.
[4] *Ber.*, 1904, **37**, 2706; 1905, **38**, 1195.

the hydrocarbon must be regarded rather as a polymeride of an eight-carbon ring compound 1:5 dimethyl *cyclo* octadiene (1:5)

$$CH_3 . C . CH_2 . CH_2 . CH$$
$$\|\qquad\qquad\|$$
$$CH . CH_2 . CH_2 . C . CH_3$$
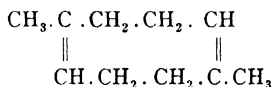
which is at present not definitely known.[1]

On exposure to light and air the rubber hydrocarbon absorbs oxygen, and is slowly converted into a brittle resinoid substance, $C_{30}H_{48}O_{10}$ [$= (C_{10}H_{16})_3 + 5O_2$], known as Spiller's resin.[2] Crude rubber may, therefore, be expected to contain more or less of this substance. Crude rubber also contains, in varying quantity, a substance insoluble in the ordinary solvents of india-rubber, but which appears to swell up enormously when subjected to their action. This substance was described by Weber as an oxygen-containing compound of the composition $C_{30}H_{68}O_{10}$ [$= 3(C_{10}H_{16}) + 10H_2O$], but Spence has shown[3] that, at all events in the case of Parà rubber, the purified substance contains nitrogen (about 5.4%), and is, at least in part, of protein nature; there is probably not more than 1 or 2% of this substance present in Parà rubber. It is, however, extremely difficult to free the substance from the last traces of rubber hydrocarbon.

The proportion of oxygen contained in commercial india-rubber is considered by Weber to afford a good criterion of the care with which the product has been collected, prepared, and stored.

The resins present in different crude rubbers differ greatly in their physical properties, and are, therefore, to some extent characteristic of the rubbers from which they are derived.[4]

Raw, or unvulcanised, india-rubber is at ordinary temperatures soft, pliable, and elastic; when heated in boiling water or subjected to mechanical working, as between masticating rollers, it becomes still softer; below 0° it hardens and, in a large measure, loses its pliability. Freshly cut surfaces are easily welded together firmly by gentle pressure. Ordinary india-rubber begins to melt at about 120°. [Gladstone and Hibbert[5] state that purified india-rubber does not

[1] Pickles (*Trans. Chem. Soc.*, 1910. 97, 1085) gives reasons for preferring the "open-chain" formula $CH_2 . CMe: CH . [CH_2]_2 . CMe: CH . [CH_2]_2 . CMe: CH . [CH_2]_2 \ldots$ to that of Harries.
[2] *J. Forts. d. Chem.*, 1865, 575.
[3] *J. Inst. Comm. Research in Tropics*, 1908, 3, 47-60.
[4] *Cf.* Ditmar, Die Analyse des Kautschuks, etc., Vienna and Leipzig, 1909. pp. 170-173.
[5] *Trans.*, 1888, 53, 686.

melt even at 200° in the absence of air, and that its solution in toluene retains its optical properties at that temperature.] After being melted it remains soft and adhesive on cooling; it hardens again when spread out in thin layers. On heating to 200° ordinary india-rubber is converted into a sticky mass which does not harden on cooling. The readiness with which these changes occur depends, to some extent, upon the source of the india-rubber. On dry distillation, india-rubber yields a variety of products, including *isoprene*, C_5H_8 (p. 163); *dipentene* or *caoutchene*, $C_{10}H_{16}$ (p. 172), and *heveene*, $C_{15}H_{24}$ or $C_{20}H_{32}$, a liquid with a faint smell and acrid taste, b. p. 315.[1]

The odour of crude india-rubber (which is really that of its impurities), is characteristic, and in many cases forms a clue to its origin.

India-rubber is insoluble in water, but is capable of absorbing up to 25% of its own weight of that liquid, and is somewhat hygroscopic. Though it can hardly be said to dissolve, in the ordinary sense, it forms a solution with chloroform, benzene, toluene, the various petroleum and shale distillates, carbon tetrachloride, carbon disulphide, etc. Similar solutions are formed with the various fatty and essential oils, fused naphthalene, phenol, etc. Although india-rubber is insoluble in absolute alcohol, the viscosity of a solution in carbon disulphide is much decreased by the addition of alcohol to the extent of 10% of the weight of carbon disulphide; such a solution, on account of its low viscosity, is often very convenient to work with. The viscosity of a rubber solution varies considerably with the solvent employed, and also with the kind of rubber, and with the amount of mechanical working to which it has been subjected. The viscosity probably bears some intimate relationship to the degree of polymerisation of the molecule, and thus to the "quality" of the rubber.[2] The readiness with which india-rubber passes into solution increases also with the amount of working (mastication) it has received.

India-rubber is a non-conductor of electricity and becomes strongly electrified when rubbed.

The sp. gr. of highly purified rubber is 0.911 at 17°; that of the technically pure substance varies from about 0.915 to about 0.931.

The india-rubber hydrocarbon, being an unsaturated compound, is very open to attack by the halogens, chlorine and bromine, additive compounds being formed in the first instance. This property of

[1] For a complete account of the products of destructive distillation see Pickles, B. A. Report, 1906.
[2] See Schidrowitz and Goldsbrough, *J. Soc. Chem. Ind.*, 1909, **28**, 3–6.

combining additively with bromine, in the proportions represented by the formula, $C_{10}H_{16}Br_4$, has been made use of by Budde,[1] who has devised a process for the direct estimation of pure rubber in raw rubber. This process has been subjected to criticism by Harries and Rimpel,[2] and others.

Ozone also forms an additive compound with india-rubber; the ozonide is a viscid oil, which solidifies to a glassy, explosive solid of the composition $C_{10}H_{16}O_6$. This substance is readily hydrolysed by distillation with steam, yielding lævulic aldehyde, lævulic acid, and lævulic aldehyde peroxide.[3]

Strong sulphuric acid chars and oxidises india-rubber on heating, and nitric acid converts it into a substance of a yellow colour, which on prolonged boiling yields oxalic, camphoric, and camphoronic acids, and other products. The oxides of nitrogen react readily with india-rubber, yielding, under certain conditions, definite products. The action of the halogens, oxides of nitrogen, and vulcanising agents (cf. p. 147 et seq.) on india-rubber, and the products obtained are fully discussed by Caspari.[4]

Analysis of Raw India-rubber.—In the analysis of raw rubber Weber recommends the estimation of the loss on washing, oily and resinous matters, combined oxygen, and mineral matter, pure india-rubber being estimated by difference. The method of procedure is as follows:

Loss on washing is estimated on as large a sample as possible, preferably between "washing-rolls" in a stream of water, the rubber being afterwards carefully dried before weighing. The figure obtained represents water, bark, and other plant tissues, sand, soluble impurities, organic and inorganic, etc. Speaking broadly, the loss on washing is in no way an indication of the quality of the crude rubber, but its amount naturally influences the cost of the purified raw rubber when ready for manufacture. For these reasons, to estimate the loss on washing, the crude product should be treated as nearly as possible in the same way as it would be by the manufacturer in preparing it for use in the factory.

Oily and resinous matters may be estimated (Weber) by extracting 5 to 10 grm. of the finely-divided, washed rubber, dried in vacuo

[1] Pharm. Zeit., 1905, 50, part 32.
[2] Gummi-Zeit., 1909, 23, 1370–1371.
[3] Harries, Ber., 1904, 37, 2708; 1905, 38, 1195.
[4] J. Soc. Chem. Ind., 1905, 24, 1274.

or in a current of carbon dioxide, with acetone, in a Soxhlet or similar extraction apparatus. Various forms of extraction apparatus have been devised for rubber extractions and similar purposes. Those forms are preferable in which the vessel containing the sample, in contact with the solvent, is continuously surrounded by the hot vapours óf the solvent, this arrangement enabling the extraction to be carried out at a somewhat higher temperature. The time required for extraction varies from 6 to about 10 hours. The acetone is distilled from the flask, the resinous residue in the flask is dried at 100°, and its weight calculated as a percentage on the washed dry rubber. The figures published by different workers for the resin content of various rubbers are by no means in agreement. Thus while, in the following table, Parà rubber is shown as containing only 1.2 to 1.3% of resins, Tankard[1] found in washed, dried Parà 2.83%, and this is not an unusual figure to obtain. The following results were published, respectively, by H. L. Terry,[2] C. O. Weber,[3] and R. Henriques.[4]

Variety of rubber	Resin, %		
	Terry	Weber	Henriques
Parà	1.2	1.3	1.3
Mozambique	3.0	3.2	3.8
Sierra Leone, red	7.4	9.7	5.8
Assam	9.3	11.3	11.3
African ball	22.8	26.1	....
African flake	41.2	63.9	....

Henriques' figures were apparently obtained by extraction with acetone. Terry's results were obtained by extracting the finely cut rubber for several hours in a Soxhlet apparatus with alcohol.

In the case of certain rubbers, which contain resins similar in character to the alban of gutta-percha (p. 158) the use of glacial acetic acid for extracting the resins, which are very sparingly soluble in acetone, has been recommended. Sierra Leone rubber is a case in point.

The *combined oxygen* is estimated, according to Weber, by carrying out a combustion of the washed, dried, acetone-extracted sample

[1] Allen's Comm. Org. Analysis, 1907, Vol. 2., Pt. 3, p. 290, footnote.
[2] *J. Soc. Chem. Ind.*, 1889, **8**, 173.
[3] *J. Soc. Chem. Ind.*, 1894, **13**, 477.
[4] Der Kautschuk and seine Quellen, Dresden, 1899, Table I.

(dried, after acetone extraction, in a current of hydrogen or carbon dioxide). The oxygen is taken as the difference between the weight of the original sample and the combined weights of carbon, hydrogen, and ash determined by combustion. By this method Weber found 1.2 to 7.4% of oxygen in various brands of rubber (ash-free). It should be noted, however, that this method takes no account of the nitrogen present in the raw rubber in the form of protein (see p. 113).

The *mineral matter* is estimated by incinerating not less than 1 grm. of the washed, dried rubber. The ash of different brands varies considerably in quantity from about 0.3% in the case of fine Parà, upwards, and the composition of the ash is to some extent characteristic of the raw rubber from which it is derived.[1]

As the result of a study and comparison of various methods[2] proposed for the complete analysis of a sample of raw rubber, Spence has suggested the following scheme as a standard method.[3]

Sampling.—Great care must be exercised in selecting the sample. Some 500 grm. should be taken from the bulk, and this should be made representative of the various biscuits, balls, etc., of which the bulk is composed. On this sample the *loss on washing* is estimated, the sample being dried in a dark chamber containing calcium chloride. To avoid the delay which complete drying in this way would entail, an accurately weighed 10 grm. sample may be taken after partial drying, cut up very finely and dried *in vacuo* over sulphuric acid at ordinary temperature.

Estimation of Resins, etc.—About 5 grm. of the washed, dry sample are weighed out, cut up very finely and extracted with boiling acetone. Parà is completely extracted in a few hours, but other rubbers may take days before extraction is complete. When complete, the acetone is distilled off, and the residue dried in the flask at 80° until its weight is constant. The extracted rubber is freed from acetone in a vacuum over sulphuric acid until constant in weight.

In rapid work the partially dried sample may be extracted at once with acetone, and the amount of moisture present may be taken as the difference between the weight of the dried extract and that of the dried rubbery residue.

Estimation of India-rubber.—1.5 grm. of the dry, extracted

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[1] Weber, Chemistry of India Rubber, 1902, pp. 12-13. Spence, *J. Inst. Comm. Research in Tropics,* 1907, **2,** 113.

[2] Enumerated in *J. Inst. Comm. Research in Tropics,* 1907, **2,** 94, footnote 6.

[3] *J. Inst. Comm. Research in Tropics,* 1907, Reprints, No. 10.

rubber is dissolved in about 100 c.c. of benzene at ordinary tempera-
ture in a flask which can be shaken vigorously at intervals to hasten
solution. Parà rubber dissolves very slowly, whereas the poorer
classes of rubber all dissolve readily within 6 to 8 hours. The solution
is made up with benzene to 200 c.c. in a graduated flask, is well shaken,
and is then filtered through a previously weighed funnel, provided with
a tightly-fitting plug of glass-wool. 100 c.c. (or less if filtration prove
to be unduly slow) of the filtrate are collected in a graduated flask,
and the remainder of the solution is then diluted with benzene, filtered,
the residue on the filter (consisting of insoluble impurities) well washed
with benzene and finally with alcohol, dried at 65° and finally *in vacuo*
over sulphuric acid, until constant in weight. The amount of *insoluble
impurities* thus arrived at includes the insoluble substance referred to
on p. 121. The 100 c.c. of benzene solution are transferred to a
weighed Erlenmeyer flask, the benzene is distilled off, the last traces
in a current of carbon dioxide, and the flask is dried *in vacuo* over
paraffin and sulphuric acid until constant in weight. The increase
in weight represents the amount of pure rubber in the sample.

Nitrogen is estimated in the washed, dry sample by Kjeldahl's
method. Whether it is legitimate to use the factor 6.25 and call the
product protein is doubtful. It is certainly not so in the case of
unwashed rubber, in which nitrogen is present in other forms than
that of protein.[1]

Mineral matter is estimated in 4 to 5 grm. of the sample, by in-
cineration in a platinum crucible, the matter being introduced into
the crucible a small piece at a time. The presence of the following
constituents should be looked for: iron, aluminium, calcium, mag-
nesium, chlorides, sulphates, and phosphates, as these may give some
clue to the source of the sample (cf. p. 107).

The results of an analysis should be expressed as percentages on the
washed, dried sample. Such results of analysis are not sufficient in
themselves to permit of a full valuation of the rubber sample, and
various suggestions have been made for supplementing the chemical
analysis by physical tests—of tensile strength, resiliency, viscosity of
solutions, etc. Agreement has not, however, been arrived at on this
subject.[2]

The only attempt made to distinguish chemically between the quality

[1] Spence.
[2] For information on these points, the reader should refer to Schidrowitz, *Ind.-rubber J.*,
1909, 37, 313, 381, 521.

of the actual rubber in different samples is that of Schneider.[1] 2 to
4 grm. of the dry rubber are dissolved in chloroform (about 300 c.c.),
and the solution is filtered from insoluble matter through silk gauze.
The residue is washed, dried, and weighed.   An aliquot portion of the
filtrate is heated to about 60°, absolute alcohol is added, the liquid
being kept continually stirred, until a permanent cloudiness is produced.
On standing, a precipitate of what Schneider terms 'α-caoutchouc,
representing the most valuable fraction of the rubber, separates, and
this is filtered off through silk gauze, dried in a current of hydrogen,
and weighed.   To the filtrate an excess of absolute alcohol is added
when a further precipitation of rubber occurs.   This fraction, known
as β-caoutchouc, is filtered off as before, washed, dried, and weighed.
The final filtrate is evaporated to dryness on the water-bath, and the
residue is extracted several times with absolute alcohol in order to re-
move resins, which are estimated by evaporating the alcoholic extract
to dryness and weighing the residue.   The residue insoluble in alcohol
is also dried and weighed; it constitutes the least valuable portion of the
rubber and is known as γ-caoutchouc.   The proportions in which
these three fractions are present are supposed to determine the quality
of the rubber.   The method should, however, be used with caution in
the case of unknown products, since oxygen-containing rubber gives
abnormal results. [2]

The following analyses by the Schneider method have been placed
on record by D. Morris (1903):

	Rubber from	
	British Guiana, %	Dominica, %
Loss on washing	17.00	8.22
α-Caoutchouc	83.00	80.14
β-Caoutchouc	0.00	0.00
γ-Caoutchouc	10.34	3.19
Protein	1.14	4.44
Resins	2.72	10.15
Ash	1.82	1.58

[1] *Gummi-Zeit.*, 1903, **17**, 874; Lunge, Chem. Tech. Untersuchungsmethoden, 5th ed., **3**, p. 320.
[2] *Gummi-Zeit.*, 1904, **18**, 461.

The process is open to objection on account of its highly empirical nature.

Analysis of Unvulcanised Rubber Mixings.—This is carried out in general on the same lines as that of vulcanised samples.

The difficulty attending the application of the alcoholic sodium hydroxide process for the estimation of fatty substitutes (p. 124) to the case of unvulcanised samples consisting of soft rubber and substitutes, is overcome by Henriques in the following manner: 5 grm. of the sample are heated for 1 hour with 25 c.c. of benzene, in a flask fitted with reflux condenser, and the flask and contents are allowed to stand overnight. 25 c.c. of N alkali are added, and the boiling is repeated for 4 hours.* The solvents are driven off on a water-bath, and the residue rinsed into a large basin with hot water. The mass is extracted several times with boiling water, the alkaline washings being poured off, and the residual rubber is kneaded in water and extracted until the washings are no longer alkaline; it is then dried at 100° and weighed, the loss in weight representing the fatty substitute present.

Vulcanised India-rubber.—When heated with sulphur or subjected to the action of chloride of sulphur (S_2Cl_2) at ordinary temperatures, india-rubber undergoes a remarkable change in properties. The product of these reactions, which is known as "vulcanised rubber," represents the form in which india-rubber almost invariably comes into use, there being but few purposes for which raw or unvulcanised rubber can be employed, for which the vulcanised product is not more suitable. Vulcanised rubber is therefore manufactured on an enormous scale. According to C. O. Weber the vulcanisation of rubber by means of sulphur is due to the formation of a continuous series of so-called "polyprene" sulphides, ranging from $(C_{10}H_{16})_{10}S$ to $C_{10}H_{16}S_2$. Th. Budde has recently, however, drawn attention to the possibility that $(C_{10}H_{16})_{10}$ S does not represent the lowest degree of sulphuration of the rubber molecule.[1] The degree of sulphuration attained is dependent, in any given case, on the temperature and time allowed for the process, and on the proportion of sulphur employed.[2] With the pure india-rubber hydrocarbon there is no formation of hydrogen sulphide, and the production of this gas during vulcanisation

[1] *Gummi-Zeit.*, 1909, **23**, 1143–1144.
[2] On the subject of vulcanisation, see *J. Soc. Chem. Ind.*, 1894, **13**, 11, 473; 1895, **14**, 436; 1902, **21**, 712; *Chem. Zeit.*, 1894, **18**, 701; 1895, **19**, 235, 382, 1918; *Gummi-Zeit.*, 1900, **14**, 17, 33; 1902, **16**, 561–564; 1910, **24**, 1211.

in any given instance is due to the occurrence of some by-reaction. Sulphur "carriers" are largely employed for accelerating and facilitating vulcanisation. Those in most common use are antimony pentasulphide, zinc sulphide, litharge, white lead, basic sulphate of lead, lead thiosulphate, lime, and magnesia. Vulcanisation by means of metallic iodides (e. g., antimony iodide) has also been employed. In Parkes' cold process, the articles to be vulcanised are immersed in a solution of 2.5 parts of sulphur chloride (S_2Cl_2) in 100 parts of carbon disulphide, or, in the case of waterproof fabrics, the surface of the material is moistened with the solution. The sulphur chloride used should be as nearly as possible pure S_2Cl_2; it should, in particular, be free from excess of chlorine, the presence of which gives rise to a brittle product on vulcanisation. The action in Parkes' process is held by C. A. Burghardt to consist in the substitution of sulphur for a portion of the hydrogen of the rubber hydrocarbon, hydrogen chloride being simultaneously formed. Weber, however, regards the process as one of simple addition, and postulates a series of chlorosulphides analogous to the sulphides of hot vulcanisation.[1] India-rubber vulcanised by Parkes' process ("cold-cured" rubber) always contains both chlorine and sulphur.

Gerard's process of vulcanisation consists in soaking the rubber for some hours in a solution of potassium pentasulphide (sp. gr. 1.25) heated at 140°, after which it is washed and dried. Pure "hot-vulcanised" india-rubber is of a greyish colour and is not appreciably adhesive at cut surfaces. It remains elastic and pliable down to fairly low temperatures. Unlike raw rubber, vulcanised rubber does not absorb any appreciable quantity of water and only swells up, without dissolving, in the ordinary solvents of india-rubber. It slowly absorbs atmospheric oxygen, and in an atmosphere of carbon dioxide takes up about its own volume of the gas. Vulcanised rubber usually contains a portion of its sulphur in the free state. This can be partly removed by boiling the rubber with sodium hydroxide solution, a treatment which sometimes assists in preventing the rubber from becoming hard and brittle.

Analysis of Vulcanised India-rubber.—The insolubility of vulcanised rubber in ordinary solvents renders inapplicable to its analysis the processes employed in the case of raw rubber. The complete analysis of a complex india-rubber article by physical and

[1] Chem. of Ind.-R., 1902, p. 97 et seq.

chemical tests is a very tedious operation. Fortunately, it is rarely required. It may become necessary in such instances as the investigation of the causes of premature decay or unexpected breakdown of manufactured rubber. Physical tests are often of little assistance in such cases

As is well known, india-rubber goods are rarely manufactured from india-rubber only, and generally contain one or more of the following substances in admixture: mineral matters, rubber substitutes or surrogates (vulcanised, oxidised, or polymerised oils), recovered rubber, ground waste rubber, bituminous substances (asphalt, pitch, etc.), resins, rosin oil, fatty and mineral oils, albumin and paraffin-wax.

There are many difficulties to be overcome in the analysis of vulcanised rubber. Substances added to the rubber before vulcanisation are liable to undergo chemical changes when heated in presence of sulphur; and, since the analysis of rubber resolves itself into the recognition and estimation of the substances originally mixed together, the problem presented is of far greater complexity even than that of the proximate analysis of the finished article.

The difficulty of obtaining a homogeneous sample of manufactured rubber is sometimes considerable, though careful, modern, large-scale manufacture tends continually to minimise this difficulty. Fairly large quantities of the substance should be taken and reduced, by cutting, rasping, or other suitable means, to a very fine state of division.

The *sp. gr.* of india-rubber is of little or no value in judging of its purity or quality. Samples which float on water are usually free from any notable admixture of mineral matters, but the test is not absolute, as manufactured rubber frequently contains air vesicles. Porosity in rubber is, as a rule, a very undesirable quality, hence the addition of certain organic substances, such as tar products, which tend to reduce porosity to a minimum, is sometimes of value.

The *apparent sp. gr.* is ascertained by placing pieces of the rubber, as large as convenient, in water, and, if the pieces float, adding alcohol, stirring the mixture well after each addition. If they sink, a concentrated aqueous solution of calcium chloride or of mercuric iodide and potassium iodide (Retger's fluid) should be added, until the pieces remain suspended in the liquid, neither floating nor sinking. The sp. gr. of the liquid is then ascertained.

The *real sp. gr.* is determined by means of the sp. gr. bottle. As much as practicable of the finely divided sample is placed in the

bottle together with some distilled water, the bottle is attached to an air-pump, the occluded air removed by exhaustion, and the bottle then filled up with air-free distilled water. To obtain the rubber in a sufficiently fine state of division, a pair of laboratory mixing rollers should be used or the sample should be rasped. The latter method is quite successful, provided the rubber contains an appreciable amount of mineral matter.

From these two sp. grs. a number (p), representing the porosity ("microporosity") of the samples may be deduced by the aid of the expression:

$$p = \left[\frac{\text{real sp. gr.}}{\text{apparent sp. gr.}} - 1 \right] 1000$$

An absolutely non-porous rubber will, of course, give $p = 0$. The porosity of a sample is influenced not only by the amount, but also by the nature of the admixtures, the highest porosity—other conditions assumed equal—being shown by samples containing considerable quantities of rubber substitute and recovered rubber, or rubber waste.

The *tensile strength* and *elongation*[1] of rubber are useful mechanical tests, but necessitate somewhat complex apparatus for their exact determination. The most successful form of apparatus so far devised appears to be that of Schopper, of Leipzig.

Electrical tests of insulation resistance, high-voltage tests, and measurements of electrostatic capacity are also valuable in certain cases.[2]

Many samples of rubber are liable when exposed to light to develop superficial cracks, due to oxidation, this phenomenon being usually referred to as "*sun-cracking*." To measure this tendency, Weber suggests the use of a mixture of 20 grm. of acetone and 60 c.c. of a 20% solution of hydrogen peroxide. The solution is allowed to stand for a fortnight before being used; it will keep for a long time. Weighed strips of equal area of the sample to be tested and of the standard with which it is to be compared are immersed in the solution for at least two days, and are then withdrawn, washed with acetone and water, and dried at 100°. The increase in weight shows the amount of oxygen absorbed. The method is very suitable for the examination

[1] On the subject of the "tensile" properties of rubber, see Schidrowitz, *Ind. R. J.*, 1909, 37, 313, 381, 521; see also *Gummi-Zeit.*, 1909, 23, 1177-1179, and *Ind. R. J.*, 1909, 38, 41.
[2] *Cf.* C. O. Weber, Chem. of Ind.-R., 1902, pp. 230, 234.

of tire covers. Ditmar[1] heats the rubber sample in oxygen at 100°, and determines the loss or gain in weight incurred thereby.

The inorganic materials mixed with rubber during manufacture are used: 1. as "fillers," that is, merely to reduce the cost of the manufactured article; 2. as sulphur carriers, which hasten the vulcanisation of the rubber or influence it in some way; 3. as pigments, to give the finished article a definite colour; or 4. to heighten in the rubber some desirable physical or mechanical property. It is not, however, possible to draw a hard and fast line between these 4 classes of ingredients. Some of the sulphur carriers, for example, are as much used for their "filling" properties and for their colouring value as for any influence they have on vulcanisation. The compounding materials employed are usually practically insoluble in water, and chemically inert at temperatures ranging from 180° to 200°.

Since red lead is a hardening agent in india-rubber and is used in admixture with the "soft" brands of rubber, the presence of this inorganic material sometimes constitutes evidence in favour of the low quality of the rubber in the sample. Barium and calcium hydroxides, and magnesium oxide have a remarkable hardening effect upon rubber, and are frequently added in small quantities for this purpose.[2]

The *ash* left on the ignition of rubber articles is not a true criterion of the amount of mineral matter in the original sample. Neither do the constituents of the ash represent truly those of the original mixing. This is due to the reducing action of organic matter upon inorganic substances (as, for example, sulphates) and to the fact that part of the organic sulphur reacts with metallic oxides to form sulphides. Some compounds (such as those of antimony and mercury) volatilise more or less completely on ignition, and carbonates are more or less converted into oxides.

Notwithstanding these sources of error, an estimation of the "ash" is

[1] Anal. d. Kautschuks, etc., 1909, 239.
[2] Heinzerling and Pahl have recorded the results of an extensive research into the influence of various inorganic and organic admixtures in rubber (*J. Soc. Chem. Ind.*, 1892, 11, 536). Their results show that the quality of rubber is much improved for some purposes by the addition of certain mineral matters. Rubber vulcanised with 10% of sulphur was found to be the most elastic. All mineral and organic substances diminished the elasticity of rubber goods, while the addition of oxides of zinc, lead, magnesium and calcium, calcium carbonate, pitch and glycerin, increased their strength. Organic admixtures, such as paraffin-wax, rosin and pitch, and small quantities of oil substitutes, increased the insulating-power of rubber, but the mixtures did not resist the action of high temperatures so well as pure rubber. Certain mineral matters, such as the oxides of zinc, calcium and magnesium (the last-named only in small quantities), and calcium carbonate also increased the insulating power of rubber. Large quantities of magnesium oxide, however, and additions of vermilion and lead oxide decreased the insulating-power. Rubber containing certain organic admixtures (such as paraffin-wax, asphalt, and oil substitutes) was found to have an increased power of resisting the destructive action of oil.

of distinct value, provided the above considerations are borne in mind. The estimation should be carried out by careful ignition of 1 to 1.5 grm. of the finely divided sample in a thin layer in a porcelain dish, or large crucible, preferably with the outside unglazed; as low a temperature should be employed as possible, and the heat regulated so that the vapours given off do not inflame. The mineral matter thus obtained may then be submitted to the usual methods of analysis, but when information is desired as to the form in which the inorganic constituents exist in the rubber, it is better to isolate the mineral matter in other ways (see pp. 136).

Mineral matter is estimated by L. de Koningh[1] by leaving 5 grm. of the very finely divided sample in contact with 50 c.c. of hydrochloric acid (sp. gr. 1.16) for 1 hour in the cold, and afterward heating the liquid to 70° for 1 hour. 50 c.c. of water are then added, and the insoluble residue washed with boiling water till free from acid. The residue is dried at 105°. The weight obtained subtracted from that of the rubber taken gives the greater part of the soluble mineral matters of the sample (the rubber is dissolved to the extent of about 1%). The insoluble mineral matter, which may contain barium sulphate and silicates, is obtained by ignition of the rubber residue. Barium sulphate is soluble in hot strong sulphuric acid and may be completely reprecipitated from this solution by dilution with water.

Lobry de Bruyn[2] has put forward certain views as to the most satisfactory composition of rubber mixings for certain purposes. The reader must be referred to the original for an account of these.

Dry and Moist Heat Tests.—Taken together, these two tests are known as the "British Admiralty Test." They are sometimes useful as showing what effect heating, in contact either with air or with steam, will have upon the sample.

The dry heat test is carried out by exposing a small sample of the rubber to a temperature of 132° for a stated time, usually 2 hours, in a hot-air oven. The deterioration brought about is noted by inspection or by the application of physical tests (tensile strength and elongation) before and after heating.

The moist-heat test is applied by heating a second sample of the rubber in steam at a temperature of 160° for 4 (or 3) hours; the operation may be conducted either in a sealed glass tube or in an autoclave.

[1] J. Amer. Chem. Soc., 1897, **19**, 952.
[2] Chem. Zeit., 1894, **18**, 329.

SCHEME OF RUBBER ANALYSIS.

2 grm. of the sample are extracted with acetone (page 123).

(A) Soluble in Acetone.	(B) Residue. Extracted with pyridine.						
	(C) Soluble in Pyridine.	(D) Residue. Extracted with alcoholic potassium hydroxide.					
		(E) Soluble in Alcoholic Potassium Hydroxide.	(F) Residue. Extracted with nitro-naphthalene.				
			(G) Soluble in Nitro-naphthalene.	(H) Residue. Extracted with boiling water.			
				(I) Soluble in boiling water.	(K) Residue.		
Resinous constituents of india-rubber. Fatty oils. Mineral oils. Resin oils. Solid hydrocarbons. Resins. Free sulphur.	Tar. Pitch. Bituminous substances. Sulphur in. above.	Chlorosulphide substitutes. Sulphide substitutes. Oxidised (blown) oils. Polymerised oils. Sulphur in substitutes. Chlorine in substitutes.	India-rubber. Sulphur in india-rubber. Chlorine in india-rubber. (The total of the above 3 constituents is determined by loss.)	Starch. Dextrin.	Mineral matter. Free carbon. Fibrous materials. Sulphur in inorganic compounds.		

The steam pressure should be released very slowly at the conclusion of the test, in order to avoid breaking up the surface of the rubber, into which the steam penetrates during the test. Contamination of the sample with the copper of the autoclave should be carefully avoided, if the sample is to be examined at an interval after the test is carried out, as such contamination renders the sample liable to rapid deterioration. Samples containing rubber substitute are, as a rule, very badly deteriorated by the moist-heat test.

For the complete analysis of vulcanised rubber samples, the scheme shown on page 121, adapted by Weber from processes devised by himself, Henriques, and others, may, in general, be followed:

It is rarely necessary, however, to go through the whole scheme with any one sample. The process may be considerably shortened, for example, in the case of samples, the mineral matter of which contains no sulphur, and the detailed composition of which is not of first importance. If, in addition, the sample is of the "drab" or "red" variety, the process may be further curtailed by the omission of the pyridine extraction, since these varieties are not likely to contain tar, pitch, or bituminous matters. The method of procedure in such cases is as follows:

2 grm. of the sample are extracted with acetone (see below).		
Soluble in Acetone.	**Residue.** Extracted with alcoholic potassium hydroxide.	
	Soluble in Alcoholic Potassium Hydroxide.	**Residue** (rubber, mineral-matter, etc.).
(See previous table on p. 121.)	Chlorosulphide substitutes. Sulphide substitutes. Oxidised (blown) oils. Polymerised oils. Sulphur in substitutes. Chlorine in substitutes.	Sulphur in rubber (= S. of vulcanisation). Chlorine in rubber.

Any antimony pentasulphide present will go into solution to some extent in the alcoholic potassium hydroxide, from which it must be reprecipitated and its amount estimated.

The mineral matter should also be estimated by careful ignition: the india-rubber of the sample is then obtained by difference.

The sulphur of vulcanisation can in this case be estimated directly on a portion of the above residue from the alcoholic potassium hydroxide treatment by the method used for total sulphur (p. 139) while the *chlorine of vulcanisation* may be determined on the remainder of

the residue by one of the methods described on p. 140. Reference must, however, be had to the precautions dealt with on p. 134.

The various methods employed under the above schemes of analysis are carried out as follows:

Acetone Extraction.—2 grm. of the finely-divided sample are placed in an extraction thimble and extracted for about 10 hours (to constant weight) in a Soxhlet apparatus of about 50 c.c. capacity. (Other forms of apparatus may be employed such as those described by Weber[1] and Schidrowitz and Kaye.[2] A very useful form of apparatus is made by Müller, Orme & Co. (see Vol. 1, Introduction). Apparatus of this type insures a much more rapid extraction of the sample, the operation occupying only about 5 hours or less.) Ether should not be substituted for acetone, as it has a slight action on the non-resinous constituents of rubber. Chloroform, benzene, and carbon disulphide also dissolve unvulcanised rubber which is sometimes present in manufactured rubber articles. The amount of acetone extract may be taken, roughly speaking, as inversely proportional to the quality of the organic constituents of the rubber sample.

The general nature of the *acetone extract* (which rarely exceeds 10% of the sample) will often give sufficient indication of its composition; a complete analysis may frequently be almost impossible. A clean extract, light in colour, is obtained in the case of a sample free from substitutes and similar additions. If the extract is a more or less viscid liquid, solid hydrocarbons and solid resins are probably absent, unless their presence is masked by that of some other liquid constituent. Mineral oil usually imparts to the acetone solution a characteristic fluorescence, and its presence may be confirmed by warming the acetone extract with a small quantity of absolute alcohol, when mineral oil remains undissolved. Mineral oil may be roughly estimated in this way. Resin oils may be detected by the purple coloration obtained with carbon disulphide and stannic bromide or by the similar colour produced by acetic anhydride and sulphuric acid (Vol. II, p. 310). Mineral or resin oil may not have been added to the mixing as such, but as constituents of "reclaimed" or "recovered" rubber used. Tallow may also be present in the extract. If voluminous flakes separate from the warm alcoholic solution on cooling, solid hydrocarbons (paraffin-wax, ceresin, ozokerite) are present.

[1] Chem. of Ind.-rubber, 1902, p. 240.
[2] J. Soc. Chem. Ind., 1907, 26, 127.

Paraffin-wax tends to protect the rubber from oxidation, probably by decreasing its microporosity; it has, however, the effect of decreasing its tensile strength.   It is sometimes added in the form of *Nantusi*, a commercial preparation composed mainly of wax and elementary sulphur.

Fatty oils may be estimated approximately by Koettstorfer's process according to which the acetone extract is saponified with a known volume of standard alcoholic potassium hydroxide, the excess of alkali being afterward estimated by means of standard acid. The fatty oil may be calculated in terms of colza oil, 1 grm. of which requires for its saponification 0.172 grm. of KOH.   It should, however, be remembered that certain resins also are partially saponified by KOH.

It has been stated that a separation of the various constituents of the acetone extract may be effected by means of aqueous and alcoholic solutions of chloral hydrate of definite strength.[1]   Experience has, however, shown that the method is altogether unreliable as a quantitative one.[2]   A partial separation may be effected by means of absolute alcohol, as indicated in the following table:

SEPARATION OF ACETONE EXTRACT BY MEANS OF ALCOHOL.

Soluble in alcohol	Insoluble in alcohol
Free fatty acids. Resins (colophony). Waxes (beeswax; carnauba). Castor and blown oils.	Fatty and mineral oils (except castor and blown oils). Tar oils; solid hydrocarbons (paraffin-wax).

It is unnecessary to distinguish between castor and blown oils since they are of equal value in rubber mixtures.   The former is practically insoluble in light petroleum, the latter are readily soluble.

Weber determines the percentage of paraffin-wax by warming the acetone extract with about 50 times its weight of glacial acetic acid, and allowing the solution to cool; the wax separates out almost quantitatively and can be filtered off and weighed.[3]   •

Fatty oils if present may either have been added as such to the mixing or may be derived from the fatty substitutes present.   To a

[1] *Cf.* Weber, *J. Soc. Chem. Ind.*, 1903, **22**, 576; Allen, 1907, Vol. 2, Pt. 3, pp. 299, 300; Lunge, Chem. tech. Unt. Methn., 1905, Vol. 3, p. 353.
[2] *Cf.* Axelrod, *Gummi-Zeit.*, 1909, **23**, 845; Frank and Marckwald, *Gummi-Zeit.*, 1909, **23**, 979.
[3] Chem. of Ind.-rubber, 1902, p. 266.

slight extent added fatty oils may undergo vulcanisation and become converted into fatty substitutes during the vulcanisation of the rubber. The use of fatty oils in mixings is very little practised at the present time, mineral or rosin oils being used by preference.

Unsaponifiable oils may be estimated, according to Henriques,[1] by extracting with ether the residue obtained after treatment of the original (not acetone-extracted) sample with alcoholic sodium hydroxide. The operation is conducted by kneading the sample with ether in a mortar as long as the ether is coloured, and determining the loss in weight sustained by it.

The acetone-soluble matter varies greatly in character with the kind of rubber, and it is not often possible, when fatty oils or other foreign substances are present in the acetone extract, to ascertain the amount of extract derived from the rubber of the sample, still less to differentiate between rubber resins and added resins. After some experience it is possible to judge, with a fair amount of accuracy, from the appearance of an extract whether it does or does not contain other substances than the rubber resins. Weber states[2] that the acetone-soluble constituents of rubber are increased by some 3 to 5%, according to the kind of rubber, on hot vulcanisation. If this be borne in mind, the amount of organic acetone extract, calculated on the india-rubber of the sample, may give a clue to the class of rubber present in the sample.

The acetone extract of a sample prepared from pure Parà rubber never reaches 4.5%, although it usually exceeds 3%. Hence it would appear to be possible to decide, from the amount of the acetone extract, whether a given sample contains Parà rubber only. This test cannot, however, be regarded as conclusive, in view of the fact that it has become the practice, to a limited extent, to employ in manufacture rubbers from which a portion of the resinous constituents have been extracted, so-called de-resinified rubbers.[3]

The acetone extract contains also the *free sulphur* of the sample, though evidence has been brought forward to show that the whole of this is not extracted.[4] This point is dealt with later (p 126).

[1] *Zeit. angew. Chem.*, 1899, 802.
[2] Chem. of Ind.-rubber, 1902, p. 264.
[3] Hinrichsen and Marcusson have recently suggested [*Zeit. angew. Chem.*, 1910, **23**, 49–52; Cf. *Chem. Zeit.*, 1910, **34**, 230–231] that evidence as to the kind of raw rubber present in a sample may be obtained by observing the optical activity or inactivity of the resins. They have found that of the rubber examined only "Para" and "Ceylon Para" (i.e., *Herea rubber*) contain an optically inactive resin.
[4] Budde, *Gummi-Zeit.*, 1909, **23**, 1143–1144.

The free sulphur may be estimated in the extract, either by taking advantage of its sparing solubility in acetone, compared with that of the organic constituents of the extract, or by oxidation to sulphuric acid and estimation of the latter.

The former method is usually adopted when the sulphur crystallises from the acetone extract in well-formed crystals; when this is the case the extract is almost certainly free from solid hydrocarbons and from oily and resinous substances other than those derived from the rubber itself. The acetone is distilled off, the dried extract weighed, and the residue treated 5 times in succession with 2 c.c. of cold acetone, the liquid being poured through a small filter into a weighed flask. The organic matter dissolves, leaving the greater part of the sulphur behind. Any sulphur on the filter is washed back into the first flask with 5 c.c. of carbon disulphide. The solvents are evaporated from the 2 flasks, and the dried residues weighed. The solubility of sulphur in acetone at ordinary temperatures amounts to 5 or 6 m. g. in the 10 c.c. used;[1] this amount must therefore be deducted from the organic residue and added to the sulphur residue. "Cold-cured" goods contain only traces of free sulphur, if any.

When the acetone extract is a complex mixture, and especially if it contain hydrocarbons, the sulphur is estimated, according to Weber, by oxidising the total extract with fuming nitric acid on the water-bath, diluting with water, and precipitating the sulphate from the filtered liquid with barium chloride. Tankard has found, however,[2] that treatment with nitric acid does not suffice to destroy all the resinous matter, etc., of rubber and that the barium sulphate obtained as described in Weber's process is usually contaminated with barium carbonate from the ignition of barium salts of resin-acids.[3] It would therefore be preferable to treat the acetone extract, after oxidation with nitric acid, as above, in the same way as in the estimation of sulphur in the pyridine extract (p. 127).

Pontio recommends the estimation of free sulphur by oxidising the extract with alcoholic hydrogen peroxide and precipitating the acidified solution with barium chloride.[4]

Hübener oxidises the free sulphur in the original sample to sulphuric acid with bromine water, and estimates the sulphuric acid formed.[5]

[1] Weber, Chem. of Ind.-rubber, 1902, p. 242.
[2] Allen, 1907, Vol. 2, Pt. 3, p. 302, footnote.
[3] See also Henriques, Chem. Zeit., 1892, 16, 1595, 1623, 1644.
[4] Bull. Soc. Chim., 1909, 5, [9], 428–442.
[5] Chem. Zeit., 1909, 33, 648–649 and 662–663.

In drawing conclusions from the amount of organic matter in the acetone extract of a sample, it should be remembered that rubbers which have undergone deterioration, owing to atmospheric oxidation, contain increased amounts of acetone-soluble matters.

Pyridine Extraction.—In order to remove and estimate coal-tar, Stockholm tar, pitch, and bituminous matters generally, Weber recommends an extraction of the acetone-extracted sample with pyridine. When acetone extraction of the sample is complete the weighed flask containing the acetone extract is removed, and another containing about 60 c.c. of pyridine (b. p. 109° to 111°) is at once connected with the extraction apparatus. Extraction is begun immediately by heating the pyridine flask in an oil-bath kept at a temperature of 116° to 120°, and is continued until no more coloured matter is dissolved out from the sample. The pyridine is then distilled off on the oil-bath, the flask carefully cleaned, the extract dried at 100°, and weighed.

The extract should be carefully examined. Its general character will give an approximate idea as to its nature. Tar is a black, viscid liquid, pitch a black, ductile mass, and asphaltum a brittle, dark, brownish-maroon substance. If more than one of these substances be present, recognition is rendered very difficult, but a separation is not of any importance. It is sometimes found that the extract is of a rubbery nature, indicating that more than the bituminous matter has been extracted; considerable care must therefore be exercised before classifying the complete pyridine extract under the heading of bituminous matter. The addition of tar and pitch to rubber mixings serves the purpose of softening the rubber, and enables the mixing process to be carried through without undue heating or mechanical working, since when thus softened the rubber can readily take up large quantities of mineral matters. Such additions also assist in diminishing the "microporosity" of the rubber, and so minimising the risk of oxidation. Asphaltum is not much used for soft-rubber goods, and does not appear to possess any advantage over many other organic admixtures.

The sulphur in the pyridine extract is present in the form of organic sulphur compounds, and cannot be estimated by the method employed in the case of the complex acetone extract, since the sulpho-acids which may be produced are not precipitated by barium chloride. The extract is oxidised with fuming nitric acid on the water-bath, and when solution is complete it is transferred, by washing out with hot fuming nitric

acid, to a small porcelain basin. The liquid is concentrated to a syrup,
0.5 grm. of pure sodium acetate added, and the mixture evaporated to
dryness and ignited, small quantities of sodium nitrate being added
to assist in completing the oxidation. The cooled mass is dissolved
in hot water, the solution filtered, and the sulphate precipitated from
the filtrate, after acidification with hydrochloric acid, by addition of
barium chloride. In Pontio's process for the complete analysis of
vulcanised rubber, the bituminous matters are extracted by means of a
mixture of acetone and lavender oil.[1]

Alcoholic Sodium or Potassium Hydroxide Extraction.—The
residue from the pyridine extraction is washed with acetone to free it
from pyridine, and is then transferred to a flask. 50 c.c. of 6% alco-
holic sodium hydroxide solution are added, and the flask heated on a
boiling water-bath for 3 hours. • The liquid is then poured off through
a weighed filter and the extraction process is repeated with a fresh
quantity of 50 c.c. of alcoholic sodium hydroxide. (The sodium or
potassium hydroxide used must be free from sulphur.) The alcoholic
residual liquid is again poured off through the same weighed filter, and
the rubber washed in the flask several times with boiling water, and
finally transferred to the filter-paper and washed with hot water until
the washings are neutral to litmus-paper. In very accurate work a
correction should be made for the amount of filter-paper dissolved by
the alkaline liquid.[2] The filter-paper and contents are then dried at
100°, in a current of hydrogen or coal-gas, and weighed.

In the absence of any notable quantity of inorganic material in
the rubber, a weighed filter need not be used, but the residue on extrac-
tion may, after washing, be transferred to a weighed flask, dried at 100°
in a current of hydrogen or coal-gas, and weighed. The refinement of
drying *in vacuo* may, generally speaking, be dispensed with. The
loss in weight sustained by the sample on extraction with alcoholic
sodium or potassium hydroxide represents, with more or less accu-
racy,[3] the amount of true substitute present. To this figure must be
added, in order to obtain the amount of substitute actually added to
the mixing, that portion of the acetone extract which consists of the
acetone-soluble portion of the substitute. This consists of unvulcan-

[1] *Bull. Soc. Chim.*, 1909, **5**, [9], 428–442.
[2] *Cf.* Thal, *Chem. Zeit.*, 1898, **22**, 974.
[3] It is advisable in all cases to further examine the alcoholic potassium hydroxide extract
before returning it as " substitute," since it is found that an appreciable, and in some in-
stances a considerable, extract may be obtained from vulcanised rubber mixings which
contain no substitute whatever (see Beadle & Stevens, *Analyst*, January, 1910).

ised or partially vulcanised oil, and is not easy to estimate, particularly when it is uncertain whether fatty oils have been added as well as substitute. [But see p. 147 on "Substitutes."] The amount of rubber substitutes found should be calculated on the original sample, and afterwards, if desired, on the total organic matter of the sample.

A correction should be made for the mineral matter dissolved by the alcoholic potassium hydroxide, which amounts in some instances to quite an appreciable figure. An approximate value may usually be obtained by estimating the ash in the sample before and after extraction, but this method fails when the minerals dissolved contain golden sulphide of antimony or vermilion. These must be estimated either in the extract or by difference, using the method described on p. 134.

In order to ascertain the nature of the substitutes present in manufactured rubber, the *chlorine and sulphur in the alcoholic sodium hydroxide extract* must be estimated.[1] These values are also required to obtain a knowledge of the extent of vulcanisation of the sample. For these estimations, the alkaline alcoholic liquid, with the washings, is evaporated to about 50 c.c., and then made up to a volume of 100 c.c. The chlorine is estimated by evaporating 50 c.c. of this liquid to dryness, and igniting the residue, adding sodium nitrate to assist in the oxidation of the carbon. The residue is dissolved in water, the solution acidified with nitric acid, and any chlorine present precipitated with silver nitrate and weighed in the usual manner. The sulphur is estimated in the remaining 50 c.c. of the original solution, by first of all heating it with bromine or bromine-water on the water-bath, in order to oxidise the alkaline sulphides present, and then evaporating the liquid to a syrup, oxidising with fuming nitric acid, evaporating to dryness and igniting as before. The residue is dissolved in water, the solution filtered, and the sulphate precipitated with barium chloride.

The following deductions from the results of the above methods of analysis have been made by R. Henriques.[2] The presence of chlorine and sulphur in approximately molecular proportions (*i. e.*, about equal

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[1] According to C. O. Weber, when white substitute (chlorosulphide) is used in hot vulcanised rubber goods, as is sometimes the case, it loses more or less of its chlorine in the form of HCl, the whole of which is retained by the rubber sample, a portion of the chlorine combining with the rubber hydrocarbon to form a hydrochloride, while in the presence of litharge, calcium carbonate, etc., the remainder is taken up by the mineral matter. The dechlorination of the substitute is, however, far from complete, and the presence of chlorine in the substitute cannot escape detection.

[2] *Chem. Zeit.*, 1893, **17**, 707.

weights) in the alcoholic soda extract, indicates the presence of white substitute (chlorosulphide) or a mixture of this with blown-oil substitute. If the sulphur is considerably in excess of the chlorine then both white and brown substitutes are present in the extract, with possibly also blown-oil substitute.[1] When sulphur only is present, and no chlorine, the substitute employed is the brown variety, or a mixture of this with blown-oil substitute. If the extract is due to the "brown" substitute alone, it will contain about 10% of sulphur, whereas at most only traces of this element will be present in a blown-oil extract. The absence of both sulphur and chlorine in the extract indicates, in the presence of a substitute, that one prepared from blown or polymerised oil has been added. It is impossible to distinguish between fatty oils which have been added to the mixing, and have become vulcanised simultaneously with the rubber and so converted into fatty substitutes, and substitutes which have actually been added as such. Heil and Esch state, however,[2] that practically no vulcanisation of fatty oil occurs at ordinary vulcanisation temperatures, as shown by acetone extraction tests.

The *residue from the alcoholic sodium hydroxide extraction* is treated with some solvent to separate the india-rubber from the mineral matter. Henriques proposed to dissolve out the former by heating with boiling petroleum, fractions boiling between 140° and 250° F. being used for the purpose.[3] According to Weber, however, this solvent only attacks very lightly vulcanised rubber. The use of nitrobenzene suggested by the latter was subsequently found to be open to a similar objection, though to a smaller degree, but its greatest disadvantage lay in the fact that the resultant solutions were frequently either difficult or impossible to filter, especially if the mineral matter consisted of antimony sulphide or zinc oxide.

Axelrod finds that by the use of a petroleum distillate boiling at about 300° a complete resolution of vulcanised rubber is effected, and he has applied this observation in the estimation of the pure rubber in

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[1] But see footnote 1, p. 150.
[2] Manufacture of Rubber Goods. Griffin, 1909, p. 117.
[3] The method of extraction of the sample with boiling petroleum was suggested by Henriques for the separation and estimation of the free sulphur and sulphur of vulcanisation, and that present in the mineral constituents (*J. Soc. Chem. Ind.*, 1893, 12, 467). The method is, however, tedious, and in many cases—as, for instance, when much mineral matter is present—the solution of the rubber is incomplete. Henriques therefore abandoned the use of this solvent (*Chem. Zeit.*, 1894, 18, 411, 412 and 422–444), and found it preferable to decompose the sulphides in the finely rasped sample with acid, and to determine the sulphur of the sulphides, and that of the sulphates as described on p. 139. The residue contains sulphur in the form of sulphur of vulcanisation and insoluble sulphates (of lead and barium) which latter can be allowed for by calculation from the bases.

rubber goods as tetrabromide[1] (see p. 134). Even with this, however, it is doubtful whether complete solution can be achieved in the presence of rubber with a high coefficient of vulcanisation, such as is found in some samples containing reclaimed rubber, for example. It is important to obtain a method by which the rubber can be conveniently dissolved and separated from the mineral matter, since the incineration of the sample causes loss of various volatile constituents (mercury and antimony compounds), carbon dioxide is driven off from carbonates, carbon pigments, carbohydrates and fibre are burnt, and so on. Weber has therefore suggested the use of α-nitronaphthalene, which quickly decomposes and dissolves the rubber of samples heavily vulcanised, and gives solutions which, when diluted with benzene and allowed to stand for a few hours, filter readily and give clear filtrates.

Another disadvantage of the nitrobenzene treatment, which also applies to the nitronaphthalene method, is the carbonisation of the rubber matter at the high temperature employed when the sample under treatment contains red lead or ferric oxide. In the case of nitrobenzene, the difficulty can be avoided by the addition of a small quantity (5%) of chloroform, which reduces the temperature from 208° to about 173°.[2] In the case of nitronaphthalene, however, only an insignificant lowering of the b. p. takes place by the addition of chloroform, and Weber prefers to use a specially made air-bath,[3] standing on a tripod, and having a thin layer of fluffy asbestos fibre inside on the bottom. The weighed residue of rubber and mineral matter (from the alcoholic sodium hydroxide treatment), together with about 60 grm. of α-nitronaphthalene, are placed in a weighed wide-necked flask, which is suspended from the lid of the bath in such a way that it does not come into contact with the sides or the bottom of the bath. The temperature is kept at 180°. A higher temperature may cause carbonisation of the rubber. The solution of the rubber is usually complete in an hour, and sometimes a much less time suffices. During the heating the contents of the flask should be frequently stirred gently with a glass rod. When solution is complete the flask and its contents are allowed to cool, about 150 c.c. of benzene are added, and the liquid

[1] *Gummi-Zeit.*, 1907, 21, 1229–1231.
[2] C. O. Weber obtained, by the nitrobenzene treatment of 2 samples of manufactured rubber, a considerable amount of carbonaceous matter left with the mineral matter after the rubber had been dissolved out. The mineral matter contained lead oxide, PbO. When the samples were examined by the nitrobenzene-chloroform method, however, no carbon was obtained, and the mineral matter contained lead peroxide, PbO₂, added to the samples as red lead. At the b. p. of nitrobenzene, lead peroxide undoubtedly oxidises the india-rubber, with production of carbon and lead oxide, PbO.
[3] Obtainable from Messrs. F. Jackson & Co., 11 Half Moon Street, Manchester.

is left to stand until the mineral matter settles out.   The solution is
then filtered, the residue on the filter being finally washed with benzene,
dried at 110° for 1 hour, and weighed.

The loss of weight by the nitronaphthalene treatment represents the
india-rubber of the sample, including the sulphur and chlorine of
vulcanisation.   The nitronaphthalene solution of the india-rubber
does not, however, contain rubber as such, since this has undergone
decomposition by the treatment,[1] and cannot be recovered from the
nitronaphthalene.[2]   For this reason the sulphur and chlorine of
vulcanisation cannot be directly estimated in this solution.

Frank and Marckwald have more recently worked out a method
for the separation of the mineral matters from a sample of vulcanised
rubber, which is free from certain of the disadvantages attending the
nitronaphthalene process, but which has itself the slight drawback
of necessitating the use of somewhat special apparatus.   The process
is carried out as follows:[3] 1 grm. of the acetone-extracted sample is
placed in a stoppered glass vessel, similar in form to an ordinary
weighing-bottle, and covered with 30 c.c. of xylene; the vessel is then
placed on a suitable support in an autoclave containing xylene; heat
is applied in such a way that the pressure rises to 15 atmospheres in
about 1 hour, and the pressure is then maintained at from 15 to 18
atmospheres during from 3 to 4 hours.   The whole apparatus is then
allowed to cool, and the vessel containing the sample is removed.   If
the liquid is clear, and the mineral matter settled at the bottom of the
vessel, it is at once diluted with an equal volume of ether and well
stirred.   If, however, the liquid be turbid, from 1 to 3 c.c. of alcohol
are added to aid clarification, and the liquid is then diluted with ether
and allowed to stand overnight.   The residue, consisting of mineral
matter, carbon, and other added ingredients, is collected on a weighed
filter, washed with ether, dried, and weighed.   Pontio[4] recommends
the use of cumene at ordinary pressures, for a similar purpose, while
Hinrichsen[5] employs petroleum of high b. p., subsequently diluting the
solution with benzol before filtration.   Frank and Marckwald[6] have

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[1] The decomposition product is stated by Weber to be similar to caoutchouc, in that
it forms an additive compound with bromine, $C_{10}H_{16}Br_4$, which is quantitatively precipitated
by alcohol.

[2] The presence of gutta-percha or balata in vulcanised rubber cannot, therefore, be
detected by this method of analysis.   In rubber articles only slightly vulcanised, gutta-
percha and balata can be extracted, according to Weber, by repeated treatment of the
original sample with cold benzene, and precipitation of the benzene extract with absolute
alcohol.   These substances are not, as a rule, present in very large proportions.

[3] See *Gummi-Zeit.*, 1908, **22**, 1344–1346.

[4] *Le Caout. et la Gutta-percha*, 1909, **6**, 2752–2753.

[5] *Chem. Zeit.*, 1909, **33**, 735–736, 756–757.

[6] *Gummi-Zeit.*, 1909, **23**, 1522–1524.

criticised this method, and have suggested modifications which, when certain precautions are taken, are said to render the process a passable substitute for the xylene method when an autoclave is not available. 1 grm. of the finely divided (acetone-extracted) sample is heated in a weighed 100 c.c. flask with 25 c.c. of boiling petroleum (b. p. 230° to 260°), or of paraffin oil (sp. gr. 0.86) until the rubber is completely dissolved. This occupies from 15 minutes to 1 hour, according to the nature of the sample. The solution is allowed to cool, made up to 100 c.c. with petroleum ether, light benzine, or ether (benzene should not be used), allowed to stand until clear (from 2 to 10 hours), and filtered through a weighed filter. The mineral matter on the filter and any remaining in the flask are well washed with the solvent used for dilution, and the filter and flask are then dried and weighed. The total increase in weight of flask and filter represents the amount of mineral matter in the sample, together with any free carbon or undissolved organic matter. The mineral matter is now digested with ammonium sulphide, to remove antimony compounds if present, and then with warm, dilute hydrochloric acid to remove all soluble minerals. The residue of insoluble mineral matter and organic matter may now, after weighing, be ignited, and weighed again, any difference in weight being taken as free carbon and organic matter. During the heating with petroleum or paraffin, magnesium carbonate is partially decomposed, carbon dioxide and water being split off, while antimony pentasulphide loses some of its sulphur and is converted into trisulphide. Account must be taken of these facts in the analysis of samples containing either of these two substances. It is, moreover, by no means a certainty that the whole of the rubber present will pass into solution even after 1 hour's heating; if not, some will of course be found when the insoluble residue is ignited.

It is almost impossible at present to ascertain the proportion of "recovered rubber" in rubber goods, and very difficult to detect its presence. Although in commerce recovered rubber is known as "devulcanised rubber," Weber affirms that it not only contains the whole of the sulphur of vulcanisation of the waste rubber from which it was obtained,[1] but also undergoes further vulcanisation in the

[1] R. Henriques (*Chem. Zeit.*, **17**, 1266), however, states that in the regeneration of rubber, actual devulcanisation seems to take place by oxidation. That such is the case is, according to Henriques, shown by the fact that regenerated rubber possesses the plastic properties of natural raw rubber to some extent, and also on analysis of a "recovered" sample, a large quantity of sulphates was found to be present, and but little sulphur in organic combination. An examination by Henriques of further samples containing only about 50% of real rubber showed, however, a proportion of sulphur of vulcanisation ranging from 0.71 to 2.03%.

process of recovery, and therefore a sample containing any quantity of this material will frequently have a high "coefficient of vulcanisation" (Weber). This "coefficient" is the percentage ratio between the amounts of india-rubber and sulphur of vulcanisation of the sample. Thus, if a sample has been found to contain 50% of real rubber substance and 2% of vulcanisation sulphur, its "coefficient of vulcanisation" will be 4%. Weber suggests this coefficient as the basis for an approximate estimation of recovered rubber.

The composition and properties of recovered rubber are described on page 153.

Direct Estimation of Rubber in Vulcanised Rubber Samples.— The main point of weakness in the scheme of analysis described above is that the essentially important constituent, the rubber itself, is estimated by difference. During recent years a number of methods have been devised having for their object the direct estimation of the rubber in a sample of vulcanised rubber. The method proposed by Axelrod[1] has been found to be of value in a number of instances, although, as at present carried out, its application would appear to be limited. In common with other similar processes, based on the formation of bromine addition compounds of rubber, Axelrod's process has been subjected to criticism by Harries and Rimpel,[2] who find that whereas the whole of the rubber is assumed to be converted into an insoluble bromine derivative, there is, in fact, a portion of it which remains in solution in the liquids employed.

Axelrod's method is carried out as follows:

1 grm. of the sample is dissolved in 100 c.c. of heavy petroleum (b. p. 300°) by heating in an oil-bath in a flask fitted with a reflux condenser; 2 to 3 hours are required for complete solution. The liquid is allowed to cool, and 10 c.c. are then drawn off by means of a pipette; the flask is kept vigorously agitated while the sample is being withdrawn. The latter is run into a beaker of 300 c.c. capacity, 50 c.c. of a solution of 16 grm. of bromine and 1 grm. of iodine in 1000 c.c. of carbon tetrachloride are added, the liquid is allowed to stand for 3 to 4 hours, and 100 to 150 c.c. of 96% alcohol are then poured in, the liquid being stirred, until the solution assumes a straw-yellow colour. The precipitate, consisting of the bromine derivative, together with insoluble mineral matter, is allowed to settle, filtered

[1] *Gummi-Zeit.*, 1907, **21**, 1229–1231; cf. Budde, *Gummi-Zeit.*, 1907, **21**, 1205–1208.
[2] *Gummi-Zeit.*, 1909, **23**, 1370–1371.

through a weighed filter, washed first with a mixture of alcohol and carbon tetrachloride in equal proportions, and finally with alcohol alone, and dried, at a temperature not exceeding 60°, to constant weight. The increase in weight of the filter represents the amount of the bromide of vulcanised rubber, plus insoluble mineral matter, the greater proportion of the inorganic material having been converted into bromides soluble in alcohol. The ash of the filter and precipitate must therefore be deducted from the weight of bromide found, before multiplying the latter by the factor 314 which gives the percentage of pure rubber ($C_{10}H_{16}$) in the original sample. The factor 314 was obtained by Axelrod by the analysis of a number of samples of bromide prepared from vulcanised Parà rubber. Strictly speaking, this factor will vary according to the degree of vulcanisation of the sample, but the error introduced in extreme cases is said to be only a comparatively small one if the same factor, 314, be employed for all cases. If lead be present, the bromide should be treated with a few drops of nitric and sulphuric acids, and the excess of acid driven off by heat before igniting, in order to prevent volatilisation of the lead.

Hübener[1] criticises Axelrod's process on the grounds that if the vulcanised sample contains disulphide molecules ($C_{10}H_{16}S_2$), these will not be precipitated by bromine, being already saturated, but will remain in solution. He therefore proposes to carry out the process in the absence of any organic solvent in a manner similar to that described under Ebonite (p. 143). The suggested method is as follows:

2.5 grm. of the finely *rasped* sample are extracted with acetone in the usual way, this extraction being followed, where necessary, by extraction with dichlorhydrin (*cf.* p. 144). Of the extracted sample, dried at 60°, 0.2 grm. (or more in the case of samples of low rubber content) is placed in a flask in contact with 100 c.c. of distilled water and 5 to 10 c.c. of bromine. The flask is gently warmed on a sand-bath until action is complete, and the greater part of the bromine volatilised, the remainder of the bromine being then driven off by heating more strongly. The solid matter is filtered off and washed with hot water and, together with the filter, transferred to a 400 c.c. Erlenmeyer flask. Excess of N/10 silver nitrate is added, together with 20 c.c. of concentrated nitric acid; the flask is heated until nitric acid fumes are given off and the liquid is reduced in volume to about 15 c.c. The liquid is then diluted with water and cooled, 5 c.c.

[1] *Chem. Zeit.*, 1909, 33, 648-649 and 662-663.

of a cold saturated solution of iron alum are added, and the excess of silver titrated with $N/10$ ammonium thiocyanate. From the amount of silver used the rubber present in the precipitate potentially as tetrabromide, $C_{10}H_{16}Br_4$, is calculated. The remainder of the rubber may, for purposes of calculation, be assumed to be present as the saturated disulphide, $C_{10}H_{16}S_2$, (see p. 145), and may be found by calculation from the combined sulphur, the latter being taken as the difference between "free" sulphur and total sulphur. "Free" sulphur is found by oxidation of 0.2 grm. of the original substance with bromine and water in the manner described above, and estimation of the sulphuric acid in the filtrate by precipitation with barium chloride. If metals are present in the ash of the sample, which give sparingly soluble sulphates, they must be estimated and the corresponding amount of sulphur added to the "free" sulphur as found by the above method before calculating combined sulphur.

A. Heintz[1] has suggested the direct estimation of the caoutchouc in manufactured rubber by combustion of the rubber matter left after other organic substances have been removed, the water produced being weighed. The unsaponifiable oils, asphalt and rubber substitutes are extracted by the usual solvents, and the well-washed and thoroughly dried rubber residue burnt, the sulphur being kept back in the usual way. The amount of caoutchouc present may then be calculated from the hydrogen found on the assumption that its composition is represented by the formula $C_{10}H_{16}$. The results are only approximate.

The residue from the nitronaphthalene treatment (or from the treatment with xylene, paraffin, etc.), may contain carbohydrates, fibrous materials, mineral matters, and the sulphur of the mineral constituents. (Cork and wood refuse are now practically never used in rubber manufacture.) The residue on the filter is therefore washed with boiling water (about 200 c.c.) in small quantities at a time, which will remove all dextrin or soluble starch; these may be detected in the filtrate by means of iodine. The previous treatment with nitrobenzene or nitronaphthalene will have converted any starchy matter into soluble starch or (chiefly) dextrin. If either of these substances, which are simply filling materials, be found, the loss in weight, after drying the residue, should be noted. In order to ascertain whether dextrin or starchy matter was originally added to the rubber, a little of the sample

[1] *Chem. Zeit.*, 1902, **26**, 247.

is boiled with water for a few minutes and one or two drops of a solu-
tion of iodine are added to the cooled liquid. Dextrin is only very
rarely employed. It should be remembered that certain mineral
constituents may be soluble in water (calcium sulphate, etc.).

The residue from the treatment with boiling water should be care-
fully examined under the microscope for animal or vegetable fibres.
These when present can be separated from the mineral matter, if their
estimation be of sufficient importance, by shaking up a known weight
of the residue with chloroform. Weber recommends that the oper-
ation be carried out in a test-tube, the residue being gently shaken
with about 20 c.c. of chloroform, and the liquid then allowed to stand.
The tube is occasionally tapped to assist the separation, and when the
mineral matter has settled and the fibres have risen to the top, a
pipette containing chloroform is dipped under the surface of the
chloroform in the tube, which is then held in an inclined position, and
the chloroform in the pipette allowed to flow out. The chloroform
in the tube will overflow, carrying the fibres with it, and these should
be received in a dish, the chloroform being subsequently evaporated
and the residue of fibres weighed. The amount of fibre in the whole
residue is then calculated.

The presence of carbon (lamp-black, etc.) in the residue from the
water extraction will be recognised by its appearance. It may be
estimated in a portion of the residue by combustion with lead chromate.
Any graphite or other carbonaceous matters present will also be
included.

Henriques proposes to estimate *lamp-black* in rubber goods con-
taining only oils, rubber substitutes, and asphalt in addition, by
exhausting the substance successively with boiling alcoholic sodium
hydroxide and cold nitrobenzene, and submitting the residue to com-
bustion. India-rubber contains carbon and hydrogen in the propor-
tions $C_{10}:H_{16}$, so that any admixture of carbon with the rubber can
be determined by means of the altered proportions between the carbon
and hydrogen. Henriques' method is regarded by Weber as quite
unreliable; in cases where other carbonaceous matters, in addi-
tion to lamp-black, are present in rubber (*e. g.*, Vandyke brown,
fibrous materials, etc.), the method is obviously inapplicable. The
proportion of lamp-black present in rubber is usually not more than
1%. Weber has found that by making up a similar mixture of
mineral matters to that found in the rubber, and blending this mixture

with varying amounts of lamp-black until the shade of colour is equal
to that of the sample, an approximate estimate of the amount of
lamp-black may be formed.

The estimation of the various mineral constituents of the residue is
carried out in the usual way.[1]   According to Weber, the most usual
inorganic substances employed are: Litharge; Paris white, whiting,
zinc white (oxide); lime; barium sulphate; Orr's white, or "litho-
pone," which is a mixture mainly of zinc sulphide and barium
sulphate; "golden sulphide" of antimony; magnesia; red lead; ferric
oxide, and French chalk.   In addition to these china clay, vermilion,
plaster of Paris, gypsum or pearl white, white lead, kieselguhr and
other siliceous earths, zinc sulphide, lead sulphide, thiosulphate and
sulphate, graphite, magnesium carbonate, pumice-stone powder, glass
powder, mica, arsenious sulphide, zinc dust, aluminium powder, iron
and brass filings, and asbestos are also used.   The microscopical
examination of the mineral matter will frequently give much useful
information as to its composition.

The total sulphur in the mineral matter is estimated in the follow-
ing manner: A weighed quantity of the residue obtained above (resi-
due K, in table on page 121) is added in small quantities at a time
to about 10 c.c. of fuming nitric acid contained in a small evaporating
basin, which is covered by a clock-glass to avoid loss.   The watch-
glass on which the mineral matter is weighed out is cleaned from
the last portions of the mineral matter by means of small pieces of
moist filter-paper, which are added to the acid.   The whole is evapo-
rated to a syrup, 20 c.c. more nitric acid are added if necessary, and the
evaporation is repeated until most of the acid has been driven off.   2

[1] In some cases, as, for instance, when the mineral matter has been largely used in a
qualitative examination, the mineral matter may be best obtained for quantitative purposes
by decomposing a known weight of the original sample with hot nitric acid, evaporating the
liquid to dryness, and adding a few drops of sulphuric acid.   The excess of acid is driven
off by heating the residue on a sand-bath, and the analysis proceeded with by the ordinary
methods.   If preferred, the original rubber, after treatment with acetone, may be decom-
posed by the nitrobenzene (or nitronaphthalene) method, and the mineral matter,
obtained by filtration of the liquid, treated as desired.   Weber recommends this course
in the analysis of samples yielding easily to the nitrobenzene treatment.

The presence of copper in rubber goods is very undesirable, owing to its deleterious influ-
ence on the rubber, especially in the case of cold vulcanised (sulphur chloride) goods.   In
such cases the copper, even when present in very small quantity, is converted into cupric
chloride, which dissolves in the resinous and oily substances present in rubber goods, and
therefore permeates the whole material, and gradually hardens and destroys the rubber.
(See also Bing, *Zeit. f. Chem. u. Ind. d. Kolloide*, 1909, 4, 232–235.)

For the detection of small quantities of copper in rubber goods, C. O. Weber ignites 2 or
3 grm. of the sample in a porcelain crucible till all carbonaceous matter is destroyed.   The
ash is moistened with a few drops of nitric acid, dried, and heated to redness for a few minutes.
It is then treated with a slight excess of dilute sulphuric acid, the solution filtered and the
residue washed with a small quantity of boiling water.   The filtrate is neutralised (or left
very faintly acid) by the addition of sodium hydroxide, and tested with zinc sulphide paper.
The method is stated to be more sensitive than the ferrocyanide test, allowing of the detec-
tion of 0.007% of copper.

grm. of pure sodium acetate are now added and the contents of the basin evaporated to dryness.[1] The residue is carefully ignited, and the carbonaceous matter burnt by the addition of a few small crystals of potassium nitrate. When graphite is present, prolonged fusion may be necessary. The mass is kept fused for a short time, and after cooling is dissolved in boiling water, filtered from oxide of iron, carbonates of lead, barium, etc., and the sulphuric acid in the filtrate precipitated by the addition of hydrochloric acid and barium chloride in the usual way. The sulphur thus found is calculated first upon the mineral matter and finally upon the original sample.

For the estimation of the *sulphides* and *sulphates* in the *mineral matter*, R. Henriques[2] boils a portion of the inorganic residue with hydrochloric acid, filters, and determines the sulphur in the insoluble residue. Any soluble sulphates will be in the acid solution. The difference between the total sulphur in the mineral constituents and the sulphur present in the insoluble residue represents that present in the form of sulphides. Sulphur present as sulphates is determined in the usual manner in the insoluble residue.

Estimation of Total Sulphur.—The processes of R. Henriques and C. O. Weber are very similar, and are carried out as follows: About 2 grm. of the sample, cut up into small pieces, are treated on a warm water-bath with about 15 c.c. of pure strong nitric acid, the rubber being added to the acid in small quantities at a time. The method is then carried out as in the determination of sulphur in the mineral matter.

The following[3] is a reliable and rapid method for the determination of total sulphur in rubber and rubber goods:

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[1] It would be preferable at this stage to add a little sodium carbonate to ensure the presence of an excess of alkali, which on fusing causes the complete decomposition of any barium or lead sulphate in the inorganic matter. Henriques adds 5 grm. of a mixture of sodium carbonate and potassium nitrate (5 : 3) instead of the sodium acetate employed by Weber. Care should be taken that the melt is not too strongly alkaline or it will unduly attack the basin. Henriques treats the fused mass with water and hydrochloric acid, and evaporates the liquid to dryness to render any silica insoluble, when nitric acid is added and the liquid filtered. Any lead sulphate present is subsequently extracted from the siliceous residue by means of boiling ammonium acetate solution and added to the main quantity of liquid. The sulphate in the solution is then precipitated with barium chloride. Barium sulphate in the siliceous residue is determined as usual. Samples containing cinnabar should be treated with nitric acid as described in the text, the liquid diluted with water and filtered, and sulphuretted hydrogen passed through the solution.

In the estimation of sulphur by Henriques' process the presence, in the mineral matters of the sample, of metals capable of forming nitrates may produce deflagration, and consequent loss of sulphur, owing to the explosive violence of the reaction. Weber, therefore, considers Carius' sealed-tube method preferable (with the rubber and nitric acid), the tube being cautiously opened after one hour's heating, resealed, and then the heating continued as before. The method is very accurate, but it should be borne in mind that any insoluble residue may contain sulphur in the form of barium, calcium, or lead sulphates.

[2] *Gummi-Zeit.,* 1899, **14,** 149, 165, 183, 197.
[3] See *Gummi-Zeit.,* 1904, **18,** 730.

About 0.5 grm. of the finely divided rubber is intimately mixed with 16 grm. of sodium peroxide in a nickel crucible at least 45 mm. in height, and 50 mm. in diameter at the top. The crucible is covered by a lid through the centre of which is drilled a hole, large enough to take easily a fairly stout iron wire. The crucible is placed upon a lightly-made stand of aluminium or copper, and is stood in a beaker of at least 500 c.c. capacity, containing sufficient distilled water to surround the crucible to within about 10 mm. of the top. The beaker may be covered with a clock-glass through the centre of which a hole to take the wire has been drilled. The end of the iron wire is heated to a red heat, and is at once introduced into the mixture through the hole in the crucible lid. Rapid combustion ensues. The crucible is allowed to cool down, and the beaker then carefully tilted to allow water to flow into the crucible. The beaker must be kept covered during the process. The fused mass is completely dissolved by heating the water, the crucible, lid, etc., removed after careful washing, the solution acidified with hydrochloric acid, boiled, filtered if necessary, and the sulphate precipitated by means of barium chloride.

The sulphur of vulcanisation may now be calculated, from the results of the various sulphur estimations, by subtracting the sum of the sulphur found in various forms from the total sulphur of the sample.[1] Owing to the importance of this figure, however, it is desirable to obtain a more direct estimation. This may be done by reproducing the residue F (page 121) by means of the necessary extractions on about 1 grm. of the sample, estimating the total sulphur in the residue by the process used for the estimation of total sulphur, and subtracting from the result obtained the amount of sulphur found in the mineral matter, which gives the sulphur in the rubber.[2]

The chlorine in a sample of rubber may be estimated by Carius' well-known sealed-tube method, using about 0.3 grm. of the sample[3] together with 5 c.c. of fuming nitric acid and 1 grm. of silver nitrate. Most rubbers contain mineral matter insoluble in nitric acid, and when this is the case, the mixture of silver chloride and insoluble mineral matter may be treated with dilute sulphuric acid and metallic

[1] In the case of rubbers free from mineral matter, or of rubbers the mineral matter of which is free from sulphur, a direct determination of the sulphur of vulcanisation can be made. See also Budde, *Gummi-Zeit.*, 1909, **23**, 1143–1144.
[2] See also Budde, *Gummi-Zeit.*, 1909, **23**, 1143–1144 Hübenet, *Chem-Zeit.*, 1909, **33**, 144–145 and 155–157.
[3] Samples containing chlorosulphide substitutes must be first treated with alcoholic potassium hydroxide as already described, and the chlorine determined as above in the residue.

zinc in a platinum vessel, the liquid being frequently stirred. When the decomposition of the silver chloride is complete, the liquid is filtered or decanted from the insoluble matter, and the chloride precipitated, or titrated with silver nitrate.

A more convenient process for the estimation of chlorine consists in oxidising the rubber by very careful fusion in platinum with a mixture of two parts of sodium carbonate and one part of potassium nitrate. The product is dissolved in water, and the chloride in the filtered liquid estimated as silver chloride.[1]

A general examination of the original rubber will frequently give valuable information as to the composition of the mineral matter present, and the form in which it occurs. Generally speaking, "grey" rubber contains no colouring-matter. Red rubbers may contain antimony pentasulphide, mercuric sulphide, or ferric oxide,[2] or, in some instances, in the case of cold-vulcanised articles, red "lake" pigment. Black rubbers are either desulphurised grey, or "cut-sheet," or they contain lamp-black, pitches, or similar compounds. Water may dissolve out certain constituents, such as calcium sulphate, from the finely rasped sample. Weber found 6% of sodium carbonate in a sample of rubber. Hydrochloric acid may separate other substances. The presence of lead sulphate in rubber may be detected and its amount estimated by boiling a known weight of the finely divided (rasped) sample with ammonium acetate solution for about half an hour, and precipitating the lead from the solution after filtration. Barium sulphate when present will, of course, remain insoluble in hydrochloric acid with the siliceous portion of the mineral matter, and may be separated from the latter by fusion with alkaline carbonates in the usual way.

Carbonic acid in the mineral matter (which frequently occurs as calcium and magnesium carbonates, less frequently as lead and zinc carbonates) may be estimated in vulcanised rubber articles, by treating the finely rasped sample (cutting will not suffice) in a Geissler or similar apparatus with dilute hydrochloric acid in which a small quantity of cupric sulphate has been dissolved. The latter serves to

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[1] A similar method has been proposed for the estimation of the total sulphur in rubber, the sulphate in the filtrate being precipitated by barium chloride. The results obtained are, however, according to Tankard (Allen, 1907, Vol. 2, Pt. 3, p. 314, footnote) quite valueless, a large amount of the sulphur present being volatilised in the form of organic sulphides.

[2] Attention has been called to the possibility of antimonial contamination of aerated waters by the red rubber rings used in some kinds of bottles. The insoluble form in which antimony occurs in rubber makes it an unlikely impurity except in traces (which have indeed been found in certain waters).

retain the sulphuretted hydrogen evolved from any sulphides which may be present. In the case of non-vulcanised rubber, the caoutchouc must be removed (wholly or partially) by treatment of the sample with boiling nitrobenzene, and a portion of the powdered residue treated as above (but see p. 134). It is advisable to follow this method even in the case of vulcanised rubber.

In the case of rubbers containing carbonates and sulphides, these constituents may be estimated separately as already described, or by estimating the total gases (by loss) given off when the finely divided sample is treated with hydrochloric acid in the usual manner, and subtracting the hydrogen sulphide evolved (previously found). The difference represents the carbon dioxide in the sample.

O. Chéneau[1] has published a systematic method for the analysis of manufactured rubber, in which the usual well-known solvents suggested by Henriques and Weber for the separation and estimation of the various ingredients of rubber goods are employed. Previous to a treatment of the sample with alcoholic sodium hydroxide, Chéneau warms a weighed quantity of the rubber with dilute acetic acid to which some cane-sugar has been added. This removes calcium, lead, zinc and magnesium carbonates, lime and zinc oxide, red lead, white lead, alkalies, and any starch present in the sample. Any hydrogen sulphide evolved by the acetic acid treatment is due to the presence of ultramarine or other sulphide decomposable by acetic acid, and its amount should be estimated.

For the estimation of the *sulphides of antimony and mercury*, when occurring either alone or together in a sample of rubber, the method described by Frank and Jacobsohn[2] may be followed. The sample, cut up into small pieces, is oxidised, as in the estimation of sulphur, by a double evaporation with nitric acid. Potassium chlorate is then carefully added, and evaporation with nitric acid on the water-bath repeated several times. Finally the nitric acid is driven off by evaporation with hydrochloric acid, the residue taken up with the latter acid, the solution diluted with water and filtered hot. If unoxidised organic material should render filtration difficult, the sample is oxidised by repeated heating with fuming nitric acid and potassium chlorate in an Erlenmeyer flask. This is, however, not as a rule necessary. Insoluble mineral constituents remain on the filter and are estimated by inciner-

ation. The antimony and mercury are precipitated from the hot filtrate—after most of the acid has been driven off, and ammonium chloride added to assist precipitation—by hydrogen sulphide. The mixed sulphides are collected on a weighed filter, or in a Gooch crucible, washed in turn with alcohol, ether, carbon disulphide and ether, to remove free sulphur, dried, and weighed. The antimony sulphide is then removed by means of ammonium sulphide, and the mercury sulphide washed as before, dried, and weighed. If necessary, the antimony in the filtrate may be converted into tetroxide, by evaporation and oxidation with nitric acid, and weighed as such.

If other minerals be present in the same sample they may be estimated in the usual way in the filtrate from the mixed sulphides.

Wagner's method[1] for the estimation of antimony in vulcanised rubber is carried out as follows:

0.5 to 1.0 grm. of the finely divided sample is mixed in a porcelain crucible with about 5 times its own weight of a mixture of sodium nitrite and potassium carbonate ($1 : 4$). A layer of the mixture is also placed on the top. Heat is cautiously applied, and gradually increased until the mass fuses. Any particles of carbon remaining are oxidised by addition of potassium nitrate. The cover of the crucible should be kept on during this process. The mass is allowed to cool, dissolved in water, boiled with excess of hydrochloric acid to expel nitrous acid, filtered, and the antimony precipitated from the filtrate by means of hydrogen sulphide. If other metals be present the antimony sulphide is dissolved, after filtration, in ammonium sulphide and reprecipitated by hydrochloric acid. The sulphide is then collected on an asbestos filter, dried in a current of carbon dioxide and weighed as Sb_2S_3.

Ebonite. Vulcanite.—When the proportion of sulphur employed in vulcanising rubber is very large (e. g., 30%) and the articles are heated for a longer time and (or) at a higher temperature than necessary for the production of ordinary vulcanised rubber, a plastic mass is obtained which, on cooling, possesses the consistency of horn, and can be turned and worked in the same way. This product forms the vulcanite and ebonite of commerce.[2]

Ebonite and similar hard-rubber products frequently contain certain

[1] *Chem. Zeit.*, 1906, **20**, 638.
[2] *Balenite* is a product, intermediate between soft rubber and ebonite, obtained by heating a mixture of 10 parts of caoutchouc with 2 parts of shellac, calcined magnesia, sulphur, and antimony sulphide.

resins (such as shellac and colophony), asphalt and pitch, and other substances in admixture. According to Heinzerling and Pahl[1] the quality of hard rubber is much deteriorated by the addition of rosin oil and resin, while on the other hand asphaltum increases the strength and elasticity of the product.

Analysis of Ebonite.—Whilst highly-vulcanised samples of soft rubber are difficult to dissolve by the nitrobenzene or other process (page 134), hard-rubber goods, such as ebonite, are quite insoluble in any known solvent.

Hard rubbers are not likely to contain any admixture of fatty substitutes, although in addition to rubber and mineral matter, certain resins and pitches are frequently present. C. O. Weber (*Chemistry of India-rubber*) gives the following scheme of analysis for hard rubber:

(A) Soluble in Acetone.	(B) Residue. Extracted with epichlorhydrin.		
Rubber resins. Added resins. Free sulphur.	(C) Soluble in Epichlorhydrin.	(D) Residue. Extracted with pyridine.	
	All resins insoluble in acetone. Sulphur in above.	(E) Soluble in Pyridine.	(F) Residue.
		Bituminous substances. Pitches. Sulphur in above.	Sulphur in residue.

Separate estimations should also be made of the mineral matter (by ignition) and of the sulphur in the mineral matter. The sample is filed to a very fine powder,[2] and about 2 grm. of the well-mixed powder are extracted with hot acetone for about two days, in the manner described on page 123. This prolonged treatment in the case of hard-rubber goods is absolutely necessary to insure complete extraction.

The acetone extract usually consists largely of sulphur, and this may be estimated by oxidation with fuming nitric acid. When the amount of organic acetone extract (total acetone extract *minus* sulphur) exceeds 4% it is probable that added resinous substances are present in the sample. The detection of the particular resin or resins present is a very difficult—usually impossible—task.

The residue from the extraction with acetone is next subjected to the action of epichlorhydrin in the extraction apparatus. It is not

[1] *Verh. d. Vereins z. Beford. d. Gewerbefl.*, 1891, 415; 1892, 25. *Cf. J. Soc. Chem. Ind.* 1892, II, 530.
[2] The powdered sample should preferably be passed through a sieve having 80 to 100 meshes to the inch. The portions not passing through should then be reground and passed through the sieve again, this being repeated until all goes through the sieve.

necessary to dry the residue after extraction with acetone, a flask containing about 75 c.c. of epichlorhydrin being attached to the apparatus as soon as the first extraction is completed. The extraction with epichlorhydrin is continued for about 3 hours. The flask must be heated upon a sand-bath or asbestos-coated wire gauze, since epichlorhydrin boils at 117°. Dichlorhydrin may be used instead of epichlorhydrin, but the b. p. of the former is very high (177°) and for this reason epichlorhydrin is the preferable solvent. These two solvents dissolve a large number of resins which are partially or wholly insoluble in acetone, as, for instance, amber, copal, dammar, mastic, shellac, etc. These resins, together with acaroid, benzoin, colophony, elemi, and sandarac, which are soluble in acetone, constitute the chief resinous constituents of hard-rubber goods. Shellac and amber are those most frequently employed. The resins are soluble in alcohol, whilst the waxes and pitches (boiled tar, stearin pitch) are insoluble. The waxes (paraffin-wax, ceresin and ozokerite) are fairly soluble in acetone (page 123), the pitches being partially soluble in acetone and in cold nitrobenzene. Asphaltum and sulphuretted stearin-pitch (Callender's bitumen) are fairly soluble in warm nitrobenzene.

The epichlorhydrin is distilled from a paraffin-bath kept at about 120° to 122°, and the residue finally dried for 2 hours at 110°. Any sulphur present in the extract may be estimated by the method employed for the analysis of the pyridine extract of vulcanised rubber (page 127).

Before extracting the matter insoluble in epichlorhydrin with pyridine, the residue should be dried until free from the former solvent. The extraction with pyridine is then carried out as described on page 127, the flask being heated on a sand-bath or in an oil-bath. The pyridine is distilled from an oil-bath, and the residue heated until free from the odour of pyridine. The amount of sulphur in the extract, when required, may be estimated as described on page 127.

The *sulphur* in the insoluble residue is next estimated as in the case of total sulphur in rubber (page 139). The figure obtained gives the sulphur of vulcanisation and that present in the mineral matter.

The *bases* present in the mineral matter of the sample are estimated and calculated as follows: Lead is calculated as PbO (litharge), antimonyas the pentasulphide, and mercury as sulphide. Zinc may be present as oxide or sulphide; calcium as carbonate or sulphate; barium generally as sulphate, sometimes as carbonate; magnesium as

oxide (or carbonate). A little of the ebonite powder should be examined by heating with hydrochloric acid (1 : 3). Any evolution of hydrogen sulphide will probably be due to the presence of zinc sulphide, carbonic acid to the presence of calcium carbonate. The absence of barium from the solution obtained proves that any of this base present in the sample is in the form of sulphate. The sulphur thus found in inorganic combination is deducted from the sulphur in the insoluble residue F, when the percentage of sulphur of vulcanisation is obtained.[1]

The amount of rubber in the sample is obtained by difference.

Direct Estimation of Rubber in Ebonite.—Hübener[2] has described a method by which the percentage of rubber in a sample of ebonite may be estimated with comparative ease. On account of the great importance attaching to such a method, if of proved value, a description is given here, though it must be pointed out that the method has not yet been sufficiently discussed to warrant its unconditional acceptance (see also page 139).

0.1 grm. of the finely divided ebonite is covered with about 75 c.c. of water and 10 c.c. of bromine, and kept at a moderate temperature until the action of the bromine is complete, and most of the excess is volatilised. The remaining bromine is then driven off by increasing the temperature. The grey, flocculent solid is filtered off, and the free sulphur (oxidised to sulphuric acid) estimated in the filtrate by precipitation with barium chloride. The bromine-derivative is transferred to a flask, and heated with 10–15 c.c. of nitric acid (sp. gr. 1.4), free from halogen, in presence of excess (say 25 c.c.) of N/10 silver nitrate, until fumes are given off. The liquid is evaporated to about 15 c.c. in bulk, diluted with water, and 5 c.c. of a saturated solution of iron alum added. The excess of silver is estimated by titration with thiocyanate, and the amount of combined bromine calculated from the amount of silver used. The amount of rubber hydrocarbon present is now calculated in the following way. Since, in the treatment with bromine, all double linkages in the rubber molecule not already satisfied by sulphur become saturated with bromine, the water-insoluble precipitate may be assumed to consist potentially of two portions, viz.: *a*. Rubber hydrocarbon completely saturated by

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[1] This method cannot be said to be invariably accurate since zinc and barium may be present in two different forms, and error would thus result in the calculation. This is hardly likely to occur in the case of barium, according to C. O. Weber, but zinc may occur as oxide and as *lithopone*.

[2] *Chem. Zeit.*, 1909, 33, 144–145, 155–157.

bromine, *i. e.*, $C_{10}H_{16}Br_4$; *b*. Rubber hydrocarbon completely saturated by sulphur, $C_{10}H_{16}S_2$. Portion *a* is calculated from the amount of combined bromine, portion *b* from the sulphur of vulcanisation. The latter is taken as the difference between total sulphur, estimated by one of the ordinary methods, and free sulphur as estimated in the manner described above. When lead, calcium, or barium compounds are present in the ash, these must be estimated quantitatively and the amount of sulphur in the corresponding sulphates must be added to the free sulphur. For either these metals are present as sulphates in the original vulcanised mixing or are converted into sulphates by the action of the bromine or of the sulphuric acid formed by its interaction with the free sulphur.

RUBBER SUBSTITUTES.

The manufacture of rubber substitutes (surrogates) has been the subject of innumerable patents. A large number of these so-called substitutes have as their basis, or starting-point, some one or other of the fatty oils, which are oxidised with the formation of solid products ("factis"). Other patents describe the preparation of substitutes for india-rubber from various compositions, containing such substances as leather, cork, asbestos, gelatin and glycerin, and ichthyol oil, with which are generally incorporated linseed oil and waste rubber. It is very doubtful whether these products have any real commercial value.

Fatty substitutes (oil substitutes) for rubber are recognised in commerce in 3 varieties, namely, "white" and "brown" (black) substitutes, and "blown-oil" substitutes. They are generally yellowish elastic substances, with a slight, characteristic odour, and a moist and oily feel. They are insoluble in the usual solvents. "White substitute" is prepared by the action of sulphur monochloride (S_2Cl_2) upon the triglycerides of unsaturated fatty acids (linseed, castor, and colza oils) in the cold (100 parts oil to about 25 parts of sulphur chloride), and "brown substitute" by the action of sulphur at high temperatures upon similar triglycerides, the oils being used either in the natural state or previously oxidised (blown). Thus white substitute is a chlorosulphide, and brown substitute a sulphide, of fatty oils. "Blown-oil substitutes" are prepared by the action of air or oxygen upon oils, and they consist therefore of oxides of triglycerides. Oil

substitutes do not absorb any considerable amount of iodine, the sul-
phur chloride forming addition-products and converting the unsatu-
rated fatty acids into saturated compounds (Henriques). Substitutes
made from "blown" oils are known in the trade as "floating substi-
tutes" (because, on account of their low sp. gr., they float on water).
Substitutes made from ordinary oils are heavier than water.

R. Henriques[1] has pointed out that since glycerides of the saturated
fatty acids are indifferent to sulphur chloride, mixtures of these fats
with the ordinary oils would yield substitutes containing comparatively
small amounts of sulphur chloride, and such substitutes would give
analytical results very similar to those of substitutes prepared from
oxidised cotton-seed oil. Boiling alcohol, however, would extract
all the saturated fats from these compound substitutes, while the ordi-
nary substitutes yield nothing to alcohol. Henriques states that
saturated and unsaturated glycerides may possibly be separated by
treatment with sulphur chloride, and subsequent extraction with
alcohol.

These substitutes are not in any sense real substitutes for natural
india-rubber. Their true nature (that of fatty oils) is not changed
by the vulcanisation to which they have been subjected, they are still
triglycerides and therefore saponifiable. For this reason they cannot
withstand many of the conditions to which manufactured rubber
articles are subjected, such as high temperature steam, etc. These
products are therefore simply organic filling-materials or adulterants,
and their use is frequent because of the popular demand for cheap
articles. Moreover, some of these substitutes are very liable to
undergo spontaneous oxidation, which when begun may attack the
true rubber in a mixture, with disastrous results.

The proportion of sulphur in the fatty substitutes is very variable,
ranging from 5 to more than 17%. The amount of soluble fatty oil
and of free sulphur present should be small, since the presence of any
considerable proportion of unaltered fatty oil may cause deterioration
of the rubber containing it, whilst when a large amount of free sulphur
is present, it must be taken into consideration when the vulcanisation
of the mixture of rubber and substitute is to be carried out, or over-
vulcanisation may result. White substitutes rarely contain more than
traces of free sulphur; oxidised oil substitutes contain neither sul-
phur nor chlorine. According to Weber, a white substitute should

[1] *Chem. Zeit.*, 1893, 17, 916.

contain not more than 10% of soluble fatty matter and not less than about 8% of combined sulphur; a brown or black substitute should not contain more than 5% of soluble fatty matter, and the proportion of free sulphur should not exceed 40% of the amount of combined sulphur.

Similarity in chemical composition between samples of these substitutes does not necessarily imply equal suitability for mixing with india-rubber. The substitute added to rubber forms a kind of solid emulsion with the latter, and the finer the emulsion formed, the better is the substitute. According to C. O. Weber, the examination of a thin film of the mixture of rubber and substitute under the microscope is the only reliable test. A solution of the consistency of thin honey is obtained by dissolving a small quantity of the mixture in benzene. A small drop of this solution is placed on the end of a microscope slide, and another slide drawn rapidly across it. A thin quickly-drying film of the sample is thus obtained, and on examination under the microscope this should appear as an almost homogeneous mixture. Bad substitutes sometimes form no emulsion at all, but break up into a mass of streaky or scaly flakes.

"Brown" substitute is almost exclusively employed in those goods which are to be vulcanised by sulphur, whereas "white" substitute is generally used for cold-cured goods, *i.e.*, goods vulcanised by sulphur monochloride. Sometimes, as in the case of greyish-white gas-tubing which is "hot-vulcanised," "white" substitute is used for the sake of the colour required, but the practice is liable to be detrimental to the quality of the finished article.

The "brown" substitutes manufactured from natural and from "blown" oils (in the latter case the oil is oxidised until it has a sp. gr. of about 0.960) are equally satisfactory, and the latter variety may be distinctly superior for certain purposes; but, in the case of "white" substitutes, those prepared from "blown" oils are not so good as the natural oil products, the former being somewhat unstable in character.

The following analyses of various fatty substitutes are given by R. Henriques: [1]

[1] *Chem. Zeit.*, 1893, **17**, 634–638.

| | Commercial products | | | | | Linseed oil substitutes from | | Colza oil substitutes from | | Poppy-seed oil substitute from oxidised oil | Castor oil substitutes | | Substitute from oxidised cotton-seed oil |
| | White substitute | | | Brown substitute | | | | | | | With minimum of S_2Cl_2 | With maximum of S_2Cl_2 | |
	A[1]	B[1]	C[2]	A	B	Fresh oil	Oxidised oil	Fresh oil	Oxidised oil				
Sulphur	6.4	6.17	8.25	15.48	17.71	9.34	4.78	8.28	6.59	7.68	4.82	10.6	6.23
Chlorine	5.0	5.86	8.88	0.7	0.36	8.84	4.85	7.62	5.95	7.44	6.70	8.95	5.36
Water	0.85	1.0				3.02	0.85						
Mineral matter (ash)	0.8	5.51											
Fatty acids	90.45	73.58				79.6	81.67	86.89	87.95	74.90	85.35		
Sulphur in the fatty acids	6.12	6.45	8.15	14.14	15.20	9.88	4.06	8.34	6.54	8.32	5.32		6.44
Chlorine in the fatty acids	0.83	0.43				Trace	0.60	Trace	Trace		0.26	Trace	Trace
Iodine absorption of substitute	30.9	31.0	32.6	42.0	42.0	56.3	52.6	32.5	26.9	33.6	35.2	21.9	30.3
Iodine absorption of fatty acids	91.3	91.2	102.3	129.0	125.6	160.3	{141.2 / 121.0}	101.5	102.8	133.3	{136.2 / 147.4 / 152.1}	143.5	91.5
Acetyl number						21.0	19.6	31.0			105.6		51.3

[1] A and B, manufactured from oxidised oil.   [2] C, from natural oil.

The foregoing results show the composition of these products as obtained from various oils. The methods for the estimation of chlorine, etc., and for the identification of any particular substitute or mixture of substitutes in india-rubber, are given on pages 129 and 130. The iodine absorption of the substitutes and of their fatty acids can be used for ascertaining the nature of the oil present.

For the examination of the fatty substitutes as to their suitability for manufacturing purposes in admixture with india-rubber, the more important estimations are the free and combined sulphur and soluble fatty oil. Acetone is the best solvent to employ, and 3 to 5 grm. of the sample are extracted in a Soxhlet apparatus for 4 hours with this solvent. The acetone is evaporated from the extract, and the residue redissolved in cold acetone, when the fatty matters will in some cases dissolve, leaving the sulphur in crystals, and almost insoluble. The liquid can be filtered to get rid of the fatty matters, and the free sulphur and fatty matters may then be weighed separately. In other cases it will be found necessary to oxidise the complete acetone extract, since some lightly vulcanised oil which is only sparingly soluble in cold acetone may be carried through with the free oil and sulphur into the extract. The method of procedure in these cases is the same as that described on page 123.

As the fatty matters extracted by acetone contain a certain proportion of combined sulphur, if the amount of free sulphur found by simple separation with acetone, as above, be deducted from the total sulphur of the sample, the result is in excess of the truth, since only the sulphur combined in the insoluble substitute is reckoned as combined sulphur. The latter figure is therefore estimated directly in the acetone-extracted substitute. The same methods are employed as described under *India-rubber.*

The character of the fatty acids obtained from a fatty substitute or, in the case of rubber, isolated from the alcoholic soda extract gives a clue to the kind of substitute under examination. Thus the fatty acids from oxidised oil substitutes never contain more than traces of sulphur and chloride, the substitute itself rarely containing sulphur or chlorine in amounts exceeding 0.5%. Brown (sulphide) substitutes contain usually from 4 to 9% of sulphur, the whole of which is found in the fatty acids when isolated. Only traces, at most, of chlorine are present in brown substitutes or their fatty acids. The fatty acids of white (chlorosulphide) substitutes contain the whole of

the sulphur of the substitute, but the greater part of the chlorine is found in the alcoholic sodium hydroxide liquid on saponification. It may be estimated in this alkaline solution as described on page 141.

In certain cases the kind of substitute or substitutes can only be determined with difficulty. It has already been pointed out that when a chlorosulphide substitute has been used in a hot-vulcanised article, a large proportion of the chlorine is evolved as hydrogen chloride, and combines with the rubber of the sample, so that it is not found with the sulphur in the saponification liquors. In such a case, the substitute present may be erroneously regarded as a sulphide substitute. Estimation of the sulphur and chlorine of vulcanisation should next be made. If the rubber does not contain sufficient chlorine to be about equal to the sulphur in the alcoholic sodium hydroxide extract, the substitute present must be a sulphide (brown) substitute.[1] Cold-vulcanised (sulphur chloride) goods never yield more than mere traces of free sulphur to acetone, whilst sulphide substitutes and hot-vulcanised rubber goods contain amounts of free sulphur which will readily be detected in the acetone extract.

"**Fenton rubber**" is manufactured[2] by mixing oxidisable vegetable oils, either in the natural or in the oxidised condition, with certain proportions of tar, pitch, or creosote, placing "the mixture, either cold or previously heated together, in a bath of diluted nitric acid, and allowing it to remain for maceration—cold, or quickening the reaction by boiling —until the whole is coagulated into a tough elastic magma having the appearance and nature of caoutchouc-like substance." The product is poured upon pans and roasted for a short time, when it coagulates into a highly elastic mass like rubber in appearance, and capable of being vulcanised. A similar process, without the addition of tar, etc., was first employed by Sachs and Jonas in 1848.

Callender's bitumen is much employed for large insulated electric cables. It is similar in some respects to ordinary "brown substitute," and is manufactured by heating a mixture of stearin-pitch and sulphur under certain conditions.

"**Oxolin**" is a patent substitute prepared by the oxidation of linseed oil, with which a vegetable fibre such as hemp is impregnated, the material being then spread on trays and repeatedly exposed to the air at a

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[1] Only thin rubber surfaces are capable of being vulcanised by the cold process, so that when a rubber article of any thickness contains chlorine, it suggests the presence of a chlorosulphide substitute.
[2] Eng. Pat. 26548 of 1896.

temperature of about 45°. It is then vulcanised by heating with sulphur in the ordinary way. In elasticity and tensile strength, "oxolin" is much inferior to india-rubber. For certain purposes, however, this product may be used instead of the low brands of india-rubber.

"Velvril"[1] is a substance which is obtained by the addition of nitroricinolein (from castor oil) or nitrolinolein (from linseed oil), containing about 4 to 5% of nitrogen, to nitrocellulose of very low nitration. A homogeneous mass is thus produced, the substance obtained by using castor oil being preferable. This product is said to have given very good results, so far as elasticity and durability are concerned, and it is not more inflammable than india-rubber. "Velvril" is insoluble in benzene, carbon disulphide, and other solvents. At the temperature of boiling water, articles made with this material do not lose their shape, only becoming more supple. By greater heat and pressure, "velvril" can be moulded into any desired form.

"Recovered," "regenerated," or "reclaimed" rubber is usually manufactured from factory scraps and cuttings or old rubber articles, such as goloshes and similar goods. In one form of recovery process, the textile fabrics present are separated or destroyed by the action of diluted sulphuric acid, the product being afterward plasticised by heating in steam under pressure. Another method consists in heating the old rubber with a solution of calcium chloride, sodium hydroxide, or other reagent, grinding the rubber thus treated with mineral oil, and again heating the product. Another kind of "recovered" rubber is that obtained from the cuttings of waterproof cloth vulcanised by the cold sulphur chloride process. After the removal of the textile materials, a rubber is obtained which is only properly vulcanised on the surface, the cold process leaving the under layers almost untouched. This rubber can be worked together by pressure between hot rollers. The rubber of course still contains chlorine, and can only be properly used again for "cold-cured" articles.

A process for the reclaiming of soft vulcanised rubber by heating with steam in presence of oil (resin or amber oil) is described by C. J. Polony.[2]

The proportion of india-rubber in "reclaimed rubber" varies widely in different samples, from about 25 to (occasionally) 75%, but does not usually exceed 35 to 40%. Most samples of reclaimed rubber

[1] *J. Soc. Chem. Ind.*, 1899, **18,** 972.
[2] *Gummi-Zeit.*, 1903, **17,** 773.

contain varying amounts of oils, rubber substitutes, carbon, asphaltum, mineral matters, etc. Since, according to Weber, all reclaimed rubber contains 8% or upwards of mineral oils or even fatty oils, or a mixture of these, the recovery process also includes some method for the incorporation of these oils with the rubber. When reclaimed rubber is treated with a solvent capable of dissolving these oils, the rubber residue frequently assumes a condition very little different from that of ground rubber waste. Thus it will be seen that all reclaimed rubbers are dependent for their plasticity upon the solvent or softening action of these oils. Reclaimed rubber can therefore only find limited application, since products containing such oils are unsuitable for the manufacture of many classes of rubber goods. According to Weber, the best recovered rubber owes its great inferiority to native rubber to the fact that it undergoes further vulcanisation with the free sulphur present during the process of recovery. Rubber which has been more than once recovered contains greater proportions of combined sulphur according to the number of times it has gone through the recovery process. The addition of reclaimed rubber to india-rubber does not of necessity alter the tensile strength appreciably, but it markedly affects the elongation, in proportion to the amount present.

The analysis of reclaimed rubber is carried out by the same methods as described under *Vulcanised Rubber*. The quantity and nature of the acetone extract[1] are useful data in judging of the value of samples of reclaimed rubber. Calculated upon the india-rubber of the sample, good reclaimed rubber should give an acetone extract below 10%, although many commercial samples will be found to give at least 20%. The smaller the amount of extract, the better the sample. The presence of saponifiable oils in the acetone extract should be ascertained by the Koettstorfer process. Weber suggests that, since the kind of fatty oil present is usually unknown, a mean saponification number of 190 be taken for the purpose of calculation, when the percentage of fatty oil is obtained by the formula

$$\frac{100 \times \text{KOH required in milligrm.}}{190 \times \text{grm. of acetone extract taken.}}$$

The saponification number of the acetone extract should be **very**

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[1] C. O. Weber found a sample of reclaimed rubber to contain about 18% of Guayule rubber, which was detected by means of its characteristic resin.

low, since the presence of fatty oils in india-rubber is liable to cause serious trouble.

The physical characters of the residue from the acetone extraction are important. Many commercial samples after extraction leave a residue consisting of a crumbly mass of rubber, etc., which has practically no elasticity or plasticity. A good sample will leave an appreciably plastic residue. Reclaimed rubber which loses by extraction with acetone any valuable property it may have possessed is only useful as a "filling" material for mixing with india-rubber.

Henriques' cold nitrobenzene process for the detection of asphaltum may be used in the analysis of reclaimed rubber after the acetone extraction has been carried out. Fatty substitutes are determined by Henriques' alcoholic potassium hydroxide process (page 124). To estimate accurately the sulphur of vulcanisation in a sample of reclaimed rubber, it is necessary to estimate the sulphur in the resulting alcoholic sodium hydroxide solution The same liquid should be tested for chlorine, which when present should always be estimated.

Weber directs that the rubber left after the above extractions should be carefully dried (avoiding oxidation) and weighed out into two equal parts. The combined sulphur is estimated in one of these, whilst the other portion is used for the hot nitrobenzene process or other method for the separation of rubber and mineral matter. The latter is then examined in the usual way, the presence or absence of carbon and vegetable or animal fibres being noted.

The presence of any appreciable amount of free sulphur in reclaimed rubber is evidence of the unsatisfactory nature of the recovery process employed. Since one aim of the recovery process is to devulcanise the rubber, any method at all likely to accomplish this object would first remove most of the free sulphur. On the other hand, the removal of all but small quantities of (free) sulphur does not necessarily imply that any devulcanisation has taken place.

When rubber has been subjected to a high temperature (say 150°, or higher) during the process of recovery, it may be regarded as probable that the rubber itself will have been affected by the high temperature, and products of decomposition formed. Weber has suggested a method for the estimation of such products in reclaimed rubber by isolating them as bromine derivatives. These brominated decomposition products (containing over 60% of Br) are insoluble in alcohol and very difficultly soluble in benzene, whereas the bromine deriva-

tives of the oils present in recovered rubber are readily soluble in alcohol and benzene and mixtures of these two solvents. For the purpose of estimating these products, Weber dissolves the acetone extract (containing oils and decomposition products of rubber) in a mixture of 2 parts of benzene and 1 of absolute alcohol, and adds bromine in slight excess to the solution. The bromine compounds of any decomposition products present are precipitated and can be fil- tered off. The precipitate is washed first with the mixed solvents and finally with alcohol, and then dried at 50°. Weber found that in 8 samples of reclaimed rubber the percentage of bromine in the com- pound obtained varied from 62.5 to 67.1, so that it is necessary to estimate the bromine in the compound obtained and subtract the weight found from the total weight of the precipitate. The percentage of decomposition products can then be calculated. Three reclaimed rubbers examined by Weber, which had been prepared from the same rubber scrap with mineral oil at temperatures of 140°, 160°, and 185°, gave, respectively, the following percentages of decomposition products: 1.16; 1.86; 2.53%. The process is likely to prove useful when the cause of the deterioration of any sample of manufactured india-rubber is to be investigated.

GUTTA-PERCHA.

Gutta-percha occurs in the *latex* of various trees belonging to the *Sapotaceæ* (*e. g., Palaquium pustulata* and other species), growing in the Malay peninsula and archipelago. It is called "percha" by the natives, "gutta" being the Malay name for gum.

The extraction and purification of gutta-percha have been fully described by E. F. A. Obach.[1]

The crude gutta-percha of commerce is a reddish, marbled mass, which often contains sand, pieces of wood, bark, etc. It is said that a plastic gum, probably *balata*, is sent from London to Singapore to be mixed with the gutta-percha. The commercial product is certainly very frequently and largely adulterated. Gutta-percha is purified by thoroughly washing the fine shavings with cold and hot water, and

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[1] Cantor Lectures, *J. Soc. Arts,* 1897 and 1898; of. *J. Soc. Chem. Ind.,* 1898, **17,** 470.
According to Eng. Patent, 1896, No. 19046, the crushed stems, leaves, and twigs are extracted with light petroleum. Melted paraffin-wax may also be used for the extraction. Ramsay, (Eng. Patent, 1897, No. 17936) substitutes rosin oil for the toluene usually em- ployed (Eng. Patent, 1896, No. 654).

then kneading them into blocks. The product obtained by extracting the leaves, twigs, etc., of the gutta-percha tree is much purer than the ordinary commercial gutta-percha.[1]

Gutta-percha dissolves in all the solvents of india-rubber. It is hard, tough, and slightly elastic at the ordinary temperature, becomes pliable at 25°, and gradually softens on heating. When pure it has a sp. gr. of about 0.961. At 60° it is so plastic that it may be pressed into any shape or drawn into threads. It becomes adhesive at 100°. When boiled in water, it swells up somewhat and takes up about 5 to 6% of water, but loses this gradually on subsequent exposure to air. When exposed to air and sunlight, gutta-percha absorbs oxygen like caoutchouc, and becomes brittle. Gutta-percha is also quickly acted upon by ozone. It can be preserved in the dark or under water, especially sea-water, without undergoing any alteration. It is not attacked by alkalies nor by hydrofluoric acid, which is therefore frequently stored in bottles made of this substance. Gutta-percha is a non-conductor of electricity.

Unlike india-rubber, gutta-percha has a cellular structure, which becomes fibrous when subjected to tension. It is very porous, and hence many specimens float on water.

The action of nitrous anhydride (N_2O_3) upon gutta-percha is similar to its action upon rubber, the nitrosite, $C_{10}H_{15}N_3O_7$ (Harries' "nitrosite C."), being apparently formed. Balata also gives a nitrosite closely resembling "nitrosite C." in its chemical characters.[2]

By mixing it with sulphur and heating, gutta-percha, like rubber, may be vulcanised, and with large proportions of sulphur it yields a substance resembling ebonite. Gutta-percha is often mixed with rubber in various proportions to increase its elasticity.

Gutta-percha is largely employed for the insulation of electric wires and cables; as a filling and setting for teeth; and for surgical purposes, in the form of gutta-percha tissue. A solution of gutta-percha in chloroform, known as "*traumaticin*," is used as a substitute for collodion.

The composition of gutta-percha is exceedingly complex, and present knowledge of its chemistry is very imperfect. Payen in 1851 found gutta-percha to contain *gutta*, *alban*, and *fluavil*. More recently

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[1] On a small scale, gutta-percha may be obtained pure and colourless by extracting it with boiling alcohol, dissolving the residue in chloroform or hot benzene, decolourising the solution with animal charcoal, and then precipitating with alcohol.
[2] See Caspari, *J. Soc. Chem. Ind.*, 1905, 24, 1274.

H. Bornträger[1] found alban to consist of several distinct substances. The "albans" and "fluavils" are oxidation products of gutta.

"Gutta" has the empirical formula C_5H_8, but is probably a mixture of several polymers of this ultimate composition. On dry distillation gutta yields *isoprene*, C_5H_8 and two hydrocarbons of higher b. p., probably containing $C_{10}H_{16}$ and $C_{30}H_{48}$. According •to Ramsay, Chick, and Collingridge,[2] no compound of the formula $C_{10}H_{16}O$ is obtainable by the direct action of chromic acid on gutta, though such a substance results, with others, from the treatment of alban with oxidising agents.

Commercial gutta-percha contains from 40 to 85% of gutta. At ordinary temperatures gutta is white and soft but not elastic, while at 45° it becomes yellow and pasty, and at 100° to 110° softens, melting and boiling at 130° with decomposition. Gutta is soluble in chloroform, toluene, and carbon disulphide, but insoluble in absolute alcohol, and in ether after treatment with alcohol. Gutta oxidises in the air, and hot nitric acid decomposes it, formic acid being among the products of the reaction.

"Alban" is described as a mixture of white resins, soluble in hot alcohol. A crystalline substance containing $C_{17}H_{26}O$ and a resinous substance of the formula $C_{17}H_{28}O$ have been recognised, and a third constituent is also stated to be present.[3]

"Fluavil," $C_{40}H_{64}O_3$ (?), is a yellow amorphous resin, which softens at about 50° and boils at 105°. It dissolves in cold alcohol, in which the alban resins are practically insoluble.

Recent work by Tschirch and Müller[4] goes to show that the 3 "albans" of the gutta-percha from New Guinea are distinct from those of the Sumatra product, whilst "fluavil" is apparently a mixture of 2 compounds of different m. p. Tschirch describes the albans as compounds soluble in boiling alcohol, the fluavils as soluble in cold alcohol, and the "albanans" as insoluble in both hot and cold alcohol. India-rubber is stated to contain alban-like substances.

The following figures, showing the composition of commercial gutta-percha and balata, are given by E. F. A. Obach:[5]

[1] *Zeit. f. anal. Chem.*, 1900, **39,** 502.
[2] *J. Soc. Chem. Ind.*, 1902, **21,** 1367.
[3] See also A. Tschirch, *Arch. der Pharm.*, 1903, **241,** 481; cf. *J. Soc. Chem. Ind.*, 1903, **22,** 1250.
[4] *Arch. der Pharm.*, 1905, **243,** 114.
[5] *J. Soc. Arts*, 1897 and 1898; *J. Soc. Chem. Ind.*, 1898, **17,** 470.
Other analyses of gutta-percha from various botanical sources have been published by V. Romburgh and T. de Haas (*J. Soc. Chem. Ind.*, 1903, **22,** 752). See also *J. Soc. Chem. Ind.*, 1904, **23,** 552, for further figures.

Description of material	Percentage composition			
	Gutta	Resin	Dirt	Water
Raw Gutta-percha				
Range.......... ●..........	23.1 to 84.3	10.1 to 65.2	1.8 to 22.3	1.0 to 26.7
Cleaned Gutta-percha				
Range.....................	24.4 to 88.8	11.2 to 67.4	0.9 to 2.0	0.5 to 2.3
Sample A.................	78.1	19.2	1.5	1.2
Sample B.................	57.5	40.9	1.0	0.6
Sample C.................	52.2	45.4	1.5	0.9
Sample D.................	55.6	40.9	1.8	1.7
Hardened Gutta-percha				
Medium quality, cleaned only.	54.7	39.4	2.7	3.2
Same sample after hardening..	93.0	2.8	2.5	1.7
Balata				
Raw; average...............	43.0	39.6	10.0	7.4
Cleaned; average......	52.1	47.9		

The following figures show in fuller detail the approximate range of composition of commercial gutta-percha, according to the results of various observers: Water, 1.0 to 1.5%; dirt (woody fibre and soil) 3 to 5%; pure gutta, 30.5 to 83.5%; "alban," 7.0 to 44.5%; and "fluavil," 3.0 to 21.0%. The ash of gutta-percha rarely, if ever, exceeds 0.5%.

W. G. Berry[1] has published figures showing the acid and ester values of the resins of gutta-percha and allied substances.

The chief data for the valuation of gutta-percha are to be found in the percentage of moisture, the amount of pure gutta, and the proportion of impurities, such as dirt, etc. The larger the proportion of gutta in a sample (and therefore the smaller the amount of resin), the more valuable it is for commercial purposes. For the insulation of telegraph cables an article containing not less than 65% of gutta is required. It is stated, however, by W. A. Caspari that the resin of gutta-percha is the insulating constituent and that it is the aim of the insulated-wire maker to obtain a product containing this resin with sufficient gutta to give the desired mechanical properties.

Balata is obtained from the latex of *Mimusops balata,* a tree growing in Guiana and Brazil. The commercial product forms a leathery mass and contains oxygen. Balata has a sp. gr. of 1.044 and melts at 149°.

[1] *J. Soc. Chem. Ind.,* 1904, **23,** 529.

It contains "alban" and "fluavil," and thus resembles gutta-percha.
The pure hydrocarbon separated from balata is isomeric with those
from gutta-percha and india-rubber, and, like them, can be vulcanised.
Balata is, at ordinary temperatures, somewhat elastic, but becomes
plastic on heating (at 50°) like gutta-percha.   The composition of raw
and cleaned balata is given on page 159.   •

Formerly balata was employed for coating telegraph wires, surgical
instruments, etc.   The production of balata has recently decreased,
owing to the fact that the tree, which grows in very unhealthy dis-
tricts, is no longer cultivated and is slowly dying out.

Analysis of Gutta-percha.—For the analysis of *gutta-percha*, Marck-
wald and Frank recommend[1] that 2 grm. of the dried sample should
be dissolved in 15 c.c. of chloroform, and the clear solution poured
gradually with constant stirring, into 75 c.c. of acetone.   The *gutta*
forms a voluminous porous cake, which can be pressed out, washed
with acetone without loss, dried at 100°, and weighed.   The dirt and
insoluble matters, if not previously separated, may be determined by
passing the solution and washings through a tared filter.   Any small
particles of gutta separated by the filter may be dissolved in hot toluene
and added to the main portion.

Alcohol cannot be substituted for acetone in the above process, but
good results are obtainable by dissolving 2 grm. of gutta-percha in 10 c.c.
of chloroform and adding 100 c.c. of ether.   After standing for 24
hours, the precipitated gutta is filtered off.

H. Bornträger[2] boils 1 grm. of the sample of gutta-percha for 12
hours under a reflux condenser with 50 c.c. of benzene, filters from dirt,
etc., and washes the residue with hot benzene.   The filtrate and wash-
ings are then evaporated to 50 c.c., and mixed with 100 c.c. of ab-
solute alcohol.   After standing on the water-bath for some hours the
gutta is completely precipitated, and is filtered off, washed 3 times with
hot alcohol, dried at 100°, and weighed.   For the separation of the
resins, the filtrate should be evaporated nearly to dryness, and the resi-
due taken up with 50 c.c. of boiling absolute alcohol.   The solution is
transferred to a weighed capsule or beaker, and allowed to stand in the
cold for 24 hours.   The liquid, containing the fluavil in solution, is
decanted, and the residue of "*albans*," well washed with cold alcohol,
dried at 80°, and weighed.   The "*fluavil*" can be recovered by evapo-

[1] *Zeit. Angew. Chem.*, 1902, 1029.
[2] *Zeit. anal. Chem.*, 1900, 39, 502.

rating the alcoholic solution and drying the residue at 80°, but loss is liable to occur from volatilisation.

Chicle is the thickened latex of *Achras Sapota L.* and is obtained chiefly from Mexico. It is used chiefly in the United States for chewing-gum. 50 tons per annum are said to be used for this purpose.

Chicle is a mixture of water-soluble gum, resins, gutta, and mineral constituents.

According to Prochazha and Endemann (*J. Amer. Chem. Soc.*, **1**, 50–62), the following is a detailed analysis of the dry, cleaned chicle:

```
Arabin.....................................  10.0
Calcium.................................•.............   9.0
Sugar......................................................   5.0
Water-soluble salts of Ca, Mg, and K.........   1.0
          Total soluble in boiling water.........  ——25.00

Alban.......................................  33.75
Fluavil.....................................  22.50
Hydrocarbon (gutta) soluble in ether.........   6.00
                    insoluble in ether.......  12.75
          Total constituents insoluble in water....  ——75.00
```

Treatment with Solvents.—The gum may be precipitated from aqueous solution by means of alcohol. When quickly filtered, washed with alcohol and then with ether, and evaporated in a vacuum desiccator, protected from the light, 9% yield of gum is obtained. The reactions of the gum are as follows:

Test for carbohydrate with naphthol-sulphonic acid should show the presence of carbohydrates. Furfural should also be found present when tested with aniline acetate (see Vol. I, p. 196). The gum is optically active.

The residue from boiling water is boiled for several hours in a flask with return flow condenser with alcohol and filtered when still hot. The alcohol is coloured brown. On cooling, crystals of alban separate to the extent of about 10%. If this treatment is repeated a large number of times, more alban or varieties of the same are extracted and the alcoholic extracts become colourless. The residue is finally soluble in chloroform and may be purified by crystallisation from boiling ether.

HYDROCARBONS OF
ESSENTIAL OILS.

By T. MARTIN LOWRY, D. Sc., A. C. G. I.

Of the hydrocarbons occurring as constituents of the essential oils of plants, by far the most abundant and numerous are the *terpenes* and their immediate allies. The properties and chief sources of these hydrocarbons will be fully described in the sequel. *Paraffins* occur in a few cases only. Thus the "*abietene*" of the oil of *Pinus sabiniana* (California) is identical with *normal heptane*, C_7H_{16}. The stearoptene or solid portion of oil of rose appears to consist of the paraffin *hexadecane*, $C_{16}H_{34}$, mixed with other substances. The hydrocarbons of the *benzene* series are only rare constituents of the essential oils, with the exception of *cymene*, $C_{10}H_{14}$. *Cinnamene* or *styrene*, a hydrocarbon having the constitution of a *phenylethylene*, $C_6H_5.CH:CH_2$, occurs in small proportion in liquid storax.

By far the most numerous and important of the hydrocarbons of essential oils are the polymers of *pentine*, C_5H_8. The relationship existing between these hydrocarbons is shown by the following arrangement, which is substantially that of Wallach:

A. **Pentines or hemiterpenes,** C_5H_8; as isoprene and valerylene.

B. **Dipentines or terpenes,** $(C_5H_8)_2$ or $C_{10}H_{16}$; including pinene, limonene, fenchene, camphene, phellandrene, etc.

C. **Tripentines or sesquiterpenes,** $C_{15}H_{24}$; as cedrene and cubebene.

D. **Diterpenes,** $C_{20}H_{32}$; as colophene and copaivene.

E. **Polyterpenes,** $(C_5H_8)_n$; as the polyprene of caoutchouc.

Pentines. Hemiterpenes.

Eight compounds of the composition C_5H_8 can theoretically exist, assuming that the formulæ are all open chains.

Isoprene, which is the most interesting of the hemiterpenes, has the constitution of a β-methyl-crotonylene (*i. e.,* unsymmetrical methyl divinyl), $CH_2:(C.CH_3).CH:CH_2$, and hence belongs to the

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acetylene series (see Vol. 3). It is obtained, together with other products, by the dry distillation of caoutchouc and gutta-percha. It is a volatile liquid boiling at about $37°$, and is not affected by treatment with mercuric bromide and water. By careful management, W. A. Tilden obtained from isoprene a tetra-bromide, $C_5H_8Br_4$, as a yellowish, oily liquid which was decomposed on distillation. When isoprene is heated to about $280°$ for some hours it polymerises with formation of *dipentene*, $C_{10}H_{16}$, and colophene, $C_{20}H_{32}$. Isoprene behaves similarly with sulphuric acid, yielding a terpene and a fluorescent colophene.

On exposure to the air, isoprene absorbs oxygen and becomes converted into a white, syrupy substance, which on distillation suddenly changes, often with explosive violence, into a white amorphous mass of the composition $C_{10}H_{10}O$. Another characteristic reaction of isoprene is that of being converted into true caoutchouc or india-rubber when brought into contact with certain chemical agents, such as strong hydrochloric acid or nitrosyl chloride. Tilden has also observed the spontaneous polymerisation of isoprene (obtained from turpentine oil) into india-rubber, the inducing cause being possibly the formation of acetic or formic acid by the oxidising action of the air, the acid thus produced converting the remainder of the isoprene into caoutchouc, a reaction that would be of great commercial importance if isoprene were more readily obtainable.

Cymene. $C_{10}H_{14}$; or, $C_6H_4(CH_3)(C_3H_7)$.

Cymene is a member of the benzene series of hydrocarbons, and has the constitution of a *methyl-isopropyl-benzene*. It cannot be made to combine with hydrogen to form terpenes, though the converse action can generally be effected by careful oxidation of the terpene with iodine.

p-Cymene is the principal constituent of the oil from wild thyme (*Thymus serpyllum*), in which it occurs with thymol and smaller quantities of carvacrol and a terpene. Cymene is present in smaller proportion in the essential oils of ginger, nutmeg, citron, ajowan, cumin, thyme (*T. vulgaris*), sage, *Origanum creticum* and *Satureja hortensis* (pepper-wort). It also occurs in resin spirit and in old oil of turpentine. It was first obtained from Roman cumin oil (*cuminum cyminum*) in which it occurs with *cuminol* or *cumic aldehyde*, $(CH_3)_2CH.C_6H_4.CHO$, and from which it derives its name. It is most conveniently prepared by mixing camphor and phosphorus pent-

oxide in molecular proportions and heating gently till action commences $(C_{10}H_{16}O + P_2O_5 = C_{10}H_{14} + 2HPO_3)$. The flask is then cooled, the cymene poured off from the metaphosphoric acid, heated again with phosphorus pentoxide, and then distilled several times over sodium. Fenchone under similar conditions is converted into the isomeric ¬n-*cymene*. O-Cymene has not been found in essential oils or in their reaction products.

p-Cymene is also formed in considerable quantity by treating turpentine oil with sulphuric acid, and still more abundantly (together with ether) by heating turpentine oil with ethyl sulphate (*Compt. rend.*, 1880, **90,** 1428).

p-Cymene is a colourless, strongly refracting fluid, having an agreeable odour, recalling that of oil of lemons. It boils at 175° to 176°, and has a sp. gr. of 0.86 at 15°. When boiled in a flask for 30 or 40 hours with a large excess of strong chromic acid mixture, or until the liquid dropping from the inverted condenser no longer appears oily, cymene is oxidised with formation of acetic, paratoluic, and terephthalic acids. To detect the last product, which is characteristic, the contents of the flask are diluted with water and thoroughly cooled. The insoluble terephthalic acid is filtered off, and purified by solution in ammonia, boiling with animal charcoal, and reprecipitation by hydrochloric acid. It is insoluble in water, alcohol, ether, chloroform, or acetic acid. It sublimes without fusing. Heated with excess of soda-lime, it yields benzene and a carbonate.

According to C. R. A. Wright, the presence of cymene in an essential oil may be detected by mixing it very gradually with twice its volume of strong sulphuric acid, so as to avoid all heating. After standing 24 hours the acid is diluted with water, and the oily liquid separated and distilled in a current of steam. If the oily portion of the distillate blackens when shaken with sulphuric acid, the above treatment should be repeated. The product is then oxidised by chromic acid mixture (see above), when terephthalic acid will be obtained if cymene be present.

Terpenes, $C_{10}H_{16}$. a. General.

The terpenes are leading constituents of the majority of the essential oils of plants, in many of which they exist in greater or less proportion. Terpenes are also obtainable by the dehydrolysis of the oxygenated compounds of the composition $C_{10}H_{18}O$ contained in various natural

essential oils, and by the reduction of alcohols and ketones of the composition $C_{10}H_{16}O$.

The terpenes are all isomerides of the molecular formula $C_{10}H_{16}$. With the single exception of camphene (solid), they are colourless liquids, lighter than water, and usually volatile without decomposition. They distil unchanged in a vacuum or a current of steam. The terpenes present a close similarity in their physical properties, a fact which renders their isolation and differentiation extremely difficult. This difficulty is further increased by the tendency which the terpenes exhibit as a class to pass from one into the other under very slight provocation, and by the ability of some of them to exist in several different modifications, e. g., dextrorotatory and lævorotatory and as mixtures of these which, when in equal proportions, give rise to in-active or racemic products. As a result, the earlier investigators seldom obtained exactly the same product from two different botanical sources, and this circumstance led to the supposed discovery of innu-merable terpenes, which were generally named by adding the suffix ene to one of the botanical names of the plant from which the oil had been obtained. Personal equation, in the details of the method of preparation, further led to different descriptions being given to the product from the same plant.

A marked advance in the knowledge of terpenes and their allies was made by Berthelot, who observed that the terpene of American turpentine oil rotated the plane of a ray of polarised light to the right, while the terpene of French turpentine oil was lævorotatory. Tilden and Shenstone further distinguished between the terpenes of the *pinene* group, $C_{10}H_{16}$, boiling at 156° to 160°, constituting the chief constituents of the essential oils of the *Coniferæ* and *Labiatæ*, and the "citrenes" (now called limonenes), boiling at about 175°, constituting the greater part of the oils from the *Aurantiaceæ* and *Umbelliferæ*. In the meantime, the crystalline additive compounds formed by the terpenes with hydrochloric acid had been studied, and Tilden and his collaborators had discovered the interesting compounds of the terpenes with nitrosyl chloride (NOCl) and nitrogen trioxide. At this point, O. Wallach commenced the remarkable researches which, in conjunction with those of Brass, Conrady, Bruhl, Baeyer, Otto and Gildemeister, and others, have, since 1884, placed the knowledge of the terpenes and their allies in a new light, and rescued their chem-istry from the previous confusion. These remarkable results were for

the most part obtained by the study of the action, on the terpenes and
their allies, of water, of the halogens and their hydrogen compounds,
of oxidising agents, of nitrous acid and nitrosyl chloride, and of the
compounds which the products of the action of the last two reagents
formed with bases.

The method employed for observing the formation of the hydro-
chlorides is described on pages 173 and 181.

The formation of the *bromides* is best observed by dissolving 1
volume of the terpene in 4 volumes of alcohol and 4 of ether. The
solution is well cooled by ice, and then 0.7 volume of bromine is
slowly added. The crystalline precipitate is washed with cold alcohol
and recrystallised from ether.

The *nitroso-chlorides* of the terpenes were originally obtained by
W. A. Tilden by the action on the oils of nitrosyl chloride gas, whereby
compounds of the formula $C_{10}H_{16}NOCl$ were obtained. A more
convenient method is that of Wallach (*Annalen*, 1888, **245,** 241), who
mixes 14 c.c. of the terpene (pinene, limonene, sylvestrene) with 20 c.c.
of amyl nitrite and 34 c.c. of glacial acetic acid. This mixture is well
cooled, and half its volume of a mixture of equal volumes of glacial
acetic and fuming hydrochloric acids gradually added, allowing time
for the blue coloration to disappear before adding more of the mixed
acids. The *nitroso-bromides* may be obtained in a similar manner.

On treating the terpene nitroso-chlorides with alcoholic potash
or cautiously heating them alone, the elements of hydrochloric acid
may be removed and products of the composition $C_{10}H_{15}NO$ obtained.

By treating the terpenes with nitrogen trioxide, *terpene nitrosates*
are formed of the composition $C_{10}H_{16}NO(ONO_2)$. Wallach pre-
pares such compounds by treating a well-cooled mixture of equal
volumes of the terpene and amyl nitrite with 0.5 volume of glacial
acetic acid and 1 volume of nitric acid of 1.4 sp. gr.

On warming the nitroso-chlorides of the terpenes with excess of
piperidine, aniline, or benzylamine, in alcoholic solution, a series of bases
are formed which are applicable to the differentiation of the terpenes.

In recent years these traditional methods of investigation have been
supplemented by synthetical experiments whereby several of the most
important members of the group have been prepared artificially, and
their structure thus finally established.

The following table, showing the general characters of the terpenes
and their principal derivatives, is based on one by W. A. Tilden
(Watts' Dict. of Chemistry, **4,** page 663):

GENERAL CHARACTERS OF TERPENES.

	Pinene	Camphene	Fenchene	Limonene	Dipentene or di-limonene	Sylvestrene	Terpinolene	Terpinene	Phellandrene	Thujene
Sp. gr.	0.858 to 0.860 at 20°	0.8422 at 54°	0.864 at 20°	0.846 at 20°	0.845 at 20°	0.848 at 20°	......	0.847 at 20°	0.8558 at 16°	0.840 at 15°
Sp. rot. $[\alpha]_D$	± 43°	± 80.6°	0	+ and − 105° to 107°	0	+ 66.3	0	0	± 17.6°	......
Ref. index $[n]_D$	1.4655 at 21°	......	1.4690 at 20°	1.4746 at 20°	1.4731 at 20°	1.4757 at 20°	......	1.4846 at 20°	......	1.4714
B. p.°	156	158.5 to 159.5; m.p. 51 to 52°	160	176	178	176	185	180	170 to 172	172 to 175
Monohydrochloride, $C_{10}H_{16}$,HCl.	saturated; crystalline. m.p. 125°	crystalline; m.p. 152°	liquid	unsaturated; liquid	unsaturated; liquid	liquid	......	......	......	......
Dihydrochloride, $C_{10}H_{16}$, 2HCl, m.p.°	50[1]	......	......	50[1]	50[1]	72	50[1]	......	......	......
Dibromide, $C_{10}H_{16}Br_2$, m. p.	169°	90°	liquid	......	......	......	69°	liquid	......	......
Tetrabromide, $C_{10}H_{16}Br_4$, m. p.	......	......	liquid	104°	125° to 126°	135°	116°	liquid	......	......

GENERAL CHARACTERS OF TERPENES.—Continued.

	Pinene	Camphene	Fenchene	Limonene	Dipentene or di-limonene	Sylvestrene	Terpinolene	Terpinene	Phellandrene	Thujene
Nitrosyl-chloride, C_{10} H_{16},NOCl, m. p.	103° (Tilden)	no compound	....	100° to 106°	103° to 104°	106°	....	....	....	....
Nitrous derivative: Formula.......... M. p...................	$C_{10}H_{15}NO$ 132°	....	....	$C_{10}H_{14}N.OH$ 72°	$C_{10}H_{14}N.OH$ 93°	....	....	$C_{10}H_{16}N_2O_2$ 155°	$C_{10}H_{16}N_2O_2$ 103° to 104°	....
Benzyl-nitrolamine, $C_{10}H_{16}(NO)NH.C_7H_7$, m. p.	122°	....	....	93°(a)	109°(a)	71°	....	137°	....	....
Chief sources or modes of formation,	Turpentine and juniper oils (*Coniferæ*); sage oil (*Labiatæ*); also in lemon oil, etc.	Isomerisation of pinene. Reduction of camphor and borneol	Reduction of fenchone from fennel oil.	Oils of neroli, orange-peel, lemon, lime, and bergamot (*Aurantiaceæ*); oils of dill and caraway (*Umbelliferæ*), etc.	Isomerisation of other terpenes; elemi, turpentine and other oils.	Russian and Swedish turpentine oils (*Coniferæ*).	Isomerisation of other terpenes	Isomerisation of other terpenes.	Fennel oil, certain eucalyptus oils.	Artificially from thujene, contained in thuja oil.

1 The 4 compounds, m. p. 50°, are identical; the product in each case is dipentene dihydrochloride.

2 $[\alpha]_D + 183.5°$.

Constitution of Terpenes.—The constitutional formulæ of the terpenes have been the subject of much controversy and ingenious speculation. The drastic methods of the earlier investigators had the unfortunate result of bringing about profound changes in the plastic materials of the terpenes and led to the formulation of many erroneous and contradictory conclusions. The use of acid reagents in particular was often responsible for unsuspected isomeric changes. Later workers, profiting by the experiences of their predecessors, have relied chiefly on gentle oxidation by alkaline permanganate solutions and on synthetical experiments.

Almost without exception the terpenes may be derived from a hydrocarbon *terpane* or *menthane*, $C_{10}H_{20}$, having the constitution of a *methyl isopropyl cyclohexane*.[1]

$$CH_3.CH \Big< \begin{matrix} CH_2 - CH_2 \\ CH_2 - CH_2 \end{matrix} \Big> CH.CH \Big< \begin{matrix} CH_3 \\ CH_3 \end{matrix}$$
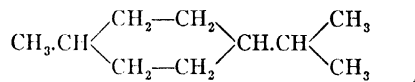
This compound is closely related to cymene, from which it may be derived by reducing the aromatic nucleus. Conversely it may be converted into cymene by oxidation.

The terpenes, $C_{10}H_{16}$, which are intermediate between cymene, $C_{10}H_{14}$, and terpane, $C_{10}H_{20}$, differ from the latter compound by 4 atoms of hydrogen in the molecule and must therefore contain, in addition to the hexamethylene ring,

I. Two double bonds, as in the **monocyclic terpenes**; or

II. A double bond and a second ring system, as in the **dicyclic terpenes**; or

III. Two additional ring systems, giving a total of 3 independent rings; no terpene of this type is definitely known, though camphene has sometimes been assigned to this group.

It may be noted that while the 3 double bonds of cymene[2] are all in the nucleus, the double bonds of the terpenes may be either in the central ring system, or in the side chains. In the latter case there is a marked tendency for the double bonds to migrate into the nucleus.

b Monocyclic Terpenes.

The following formulæ have been established fairly definitely by synthetical and other methods:

[1] The formula shows the constitution of the *p*-compound; a few of the terpenes (see Carvestrene and Sylvestrene) are derived from the *m*-isomeride.
[2] Using for convenience the Kekulé formula for benzene.

I. **Limonene** (dipentene) and

II. **Terpinolene** derived from terpineol[1] by removal of a molecule of water by means of potassium hydrogen sulphate and alcoholic sulphuric acid, respectively.

III. *β*-**Phellandrene,** synthesised by Kondakow and Schindelmeiser (*J. Pr. Ch.*, 1905, [2], **72,** 193; 1908, **75,** 141). These 3 terpenes contain 1 double bond in the nucleus and 1 in a side chain; the 2 following contain 2 double bonds in the nucleus and may therefore be described correctly as dihydro-p-cymenes.

IV. **Terpinene,** produced by means of sulphuric acid from the preceding terpenes by isomeric changes involving the transfer of a double bond from the side chain to the nucleus.

V. *α*-**Phellandrene.** Synthesised by Harries and Johnson (*Ber.*, 1905, **38,** 1832).

Somewhat separated from the above terpenes is

VI. **Sylvestrene,** the *m*-compound analogous with dipentene.

The monocyclic terpenes are for the most part characterised by the formation of tetrabromides, while the dicyclic terpenes usually form only dibromides, though they often add on 2HBr, owing to the rupture of one of the ring systems by the acid.

MONOCYCLIC TERPENES.

Terpineol.

I. Limonene (dipentene).

IV. Terpinene.

II. Terpinolene.

III. *β*-Phellandrene.

V. *α*-Phellandrene.

VI. Carvestrene (sylvestrene).

[1] Synthesised by Perkin (Trans. 1904, **85,** 654).

Limonene, $C_{10}H_{16}$.

Limonene is a very frequent constituent of essential oils, and some of the oils from the *Aurantiaceæ* are almost wholly composed of it. Besides occurring largely in these oils, limonene exists largely in the oils of some of the *Umbelliferæ*. Thus it forms about 60% of oil of dill, and is not much less abundant in oil of caraway, being in each case associated with carvone. The oil from *Erigeron canadense* is stated to consist almost entirely of limonene, which also occurs in appreciable quantity in some pine oils, in massoya oil (from the bark of *Cinnamomum kiamis*), and in the oil from jaborandi leaves.

The terpenes known as *citrene, bergamene, hesperidene, carvene*, etc., are merely limonene containing traces of impurities varying with the origin of the oils from which they are prepared. To these very persistent impurities the characteristic odours of the oils are frequently due.

The limonene in the oils from the *Aurantiaceæ* and caraway oil is chiefly dextrorotatory ($[a]_D = + 106.8°$), and the large proportion in which it is present imparts this character to these oils; but the limonene of the oils distilled from the leaves of *Pinus sylvestris* and *P. picea* (known in commerce as "Pinewood oil") is lævorotatory to an almost equal extent ($[a] = - 105°$). The oils of lemon, lime, and caraway contain a mixture of the 2 limonenes. By mixing equal parts of dextro- and lævo-limonene, an optically inactive terpene is obtained, which appears to be identical with dipentene.

Limonene is a liquid of pleasant odour, boiling at 175° to 176°, and having a sp. gr. of 0.846 at 20°. Hence it is lighter and has a higher b. p. than pinene.

Inactive limonene or dipentene[1] has been found *abundantly* in but few of the natural essential oils. It is stated to form a considerable proportion of elemi oil, in which it exists with phellandrene and traces of polyterpenes and oxygenated compounds. Wallach also found it in considerable quantity in the essential oil of the camphor-tree, and according to Brühl, it also occurs in oil of cascarilla. The oils of bay, turpentine, cardamoms, massoya, mace, bergamot, fennel, and myrtle are stated to contain more or less dipentene; but in view of the facility with which certain other terpenes (especially pinene) are converted into dipentene by the action of heat, acids, etc., the

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[1] Also described as *terpilene, terpinylene, cinene, cajeputene, isoterebenthene*, and *kautschene*.

presence of this terpene in essential oils which have been exposed to slightly abnormal conditions is only to be expected. It seems highly probable that the loss in optical activity observed in some oils by storing or heating is frequently due to the formation of inactive dipentene from various optically active terpenes. The inactive terpene is conveniently prepared from the dihydrochloride by boiling with 1 part of sodium acetate and 2 parts of glacial acetic acid for half an hour in a flask furnished with a reflux condenser. The product which was originally called terpilene is then distilled with steam, the oil which distils boiled with potassium hydroxide, redistilled, dried, and purified by fractional distillation. It has recently been synthesised by W. H. Perkin, Jr., starting from pentane tri-carboxylic acid (Trans., 1904, **85**, 654); the synthetical product differs from active limonene only in being optically inactive.

Active limonene hydrochloride, $C_{10}H_{16}HCl$, prepared by passing a stream of dry hydrochloric acid gas through dry limonene, is a liquid, b. p. 97° to 98° under 11–12 mm. pressure, sp. gr. 0.982, and $[\alpha]_D \pm 40°$.

The dihydrochloride, $C_{10}H_{16}$, 2HCl, usually known as dipentene dihydrochloride, is produced in an inactive form by the action of moist hydrogen chloride on active limonene, inactive dipentene, or active pinene. It may be prepared conveniently by mixing a solution of dipentene or limonene in glacial acetic acid, with glacial acetic acid saturated with hydrogen chloride gas. The dihydrochloride crystallises from a mixture of alcohol and ether in rhombic plates, having a peculiar odour and melting at 50°. It boils at 118° to 120° at 10 mm. pressure. It dissolves readily in alcohol, but on heating the solution an oil separates out, consisting of a mixture of dipentene and terpinene dihydrochlorides. By the method described above, dipentene can be reproduced from the dihydrochloride; but more or less *terpinene* and *terpinolene*, besides *cymene* and small quantities of a *paraffinoid hydrocarbon*, appear to be constant secondary products (Tilden and Williamson, Trans. 1893, **63**, 292).

The dihydrochloride is decomposed by boiling with water or alcoholic potassium hydroxide with formation of *terpineol*, $C_{10}H_{17}.OH$.

When the dihydrochloride is treated with a drop of a concentrated solution of ferric chloride and the mixture gently heated, a rose colouration is produced, which changes to an intense violet-red, and ultimately to blue. To obtain the reaction, which was first observed

by Riban (*Ann. Chim. Phys.*, [5], **6,** 37), it is not necessary to prepare the hydrochloride previously, but a few drops of lemon, turpentine, or other oil containing a terpene which yields dipentene dihydrochloride on treatment with moist hydrogen chloride (*e. g.*, pinene, limonene) may be stirred in a porcelain capsule with a drop of concentrated hydrochloric acid, and another drop of a strong solution of ferric chloride. As the sesquiterpenes do not form dihydrochlorides, the test may be used to detect pinene and other terpenes in presence of the former compounds.

Dipentene dihydrobromide, $C_{10}H_{16},2HBr$, is obtained by saturating glacial acetic acid with hydrogen bromide gas, and adding a solution of limonene or dipentene in glacial acetic acid. The compound separates at once in crystals, m. p. 64°, and closely resembles the dihydrochloride.

According to Baeyer, the dihydrochloride and dihydrobromide of cinene each exists in 2 isomeric forms, comparable to maleic and fumaric acids. The usually occurring or *trans*-modification of the dihydrochloride melts at 50°, whereas the *cis*-form, prepared from cineol and hydrochloric acid, melts at 25°. Similarly the *trans*-modification of the dihydrobromide melts at 64°, while the *cis*-form, prepared from cineol, melts at 39°. Both forms easily regenerate dipentene.

Active limonene tetrabromide, $C_{10}H_{16}Br_4$, is obtained by acting with bromine on limonene dissolved in 10 parts of glacial acetic acid. It separates in hemihedral rhombic crystals, which are soft and pliable, and when recrystallised from ethyl acetate melts at 104°.

The inactive (dipentene) tetrabromide, m. p. 124°, prepared from inactive dipentene or by mixing the *d*- and *l*-tetrabromides, is less readily soluble in ether.

Limonene nitrosochloride, $C_{10}H_{16}NOCl$, prepared by passing nitrosyl chloride into a solution of limonene or oil of orange-peel in 5 parts of methylated spirit, cooled to —10°, or by Wallach's method, described on page 167, separates in crystals, m. p. 103°. By boiling with alcoholic potassium hydroxide it is converted into carvoxime, $C_{10}H_{14}(N.OH)$, by elimination of a molecule of hydrogen chloride; the identity of the two products—nitroso-limonene and carvoxime—is of considerable value in deducing structural formula for limonene and for carvone.

The nitrosochloride, prepared from either dextro- or lævo-limonene,

CHARACTERS OF NITROLAMINES.

Compound	Formula	Source				
		Dextro-limonene		Lævo-limonene		Dipentene
		Rot.° $[\alpha]_D$	M. p.	Rot.° $[\alpha]_D$	M. p.	M. p.
Terpene....................	$C_{10}H_{16}$..............	+106.8	......	−105.00		
Monohydrochloride........	$C_{10}H_{16}.HCl$.........	−40.0	......	+39.5	......	
Tetrabromide............	$C_{10}H_{16}Br_4$..........	−73.27	104°	−73.45	104°	124°
α-nitrosochloride.........	$C_{10}H_{16}NOCl$........	+313.4	103–104°	−314.8	103–104°	101°
β-nitrosochloride.........	$C_{10}H_{16}NOCl$........	+240.3	105–106°	−242.2	100°	
α-nitrolpiperidine........	$C_{10}H_{16}NO.N(C_5H_{10})$.....	+67.75	94°	−67.60	94°	154°
β-nitrolpiperidine........	$C_{10}H_{16}NO.N(C_5H_{10})$.....	−60.48	111°	+60.18	110°	152°
α-nitrolaniline............	$C_{10}H_{16}NO.NHPh$........	......	112°	......	112°	125°
β-nitrolaniline............	$C_{10}H_{16}NO.NHPh$........	......	153°	......	153°	149°
α-nitrolbenzylamine......	$C_{10}H_{16}.NO.NH(C_7H_7)$.....	+163.8	93°	−163.6	93°	110°
α-nitrolbenzylamine hydrochloride.	$C_{10}H_{16}.NO.NH(C_7H_7).HCl$.....	−82.26	......	+83.06		
Carvoxime................	$C_{10}H_{14}.NOH$........	−39.34	72°	+39.71	72°	93°
Benzoyl-carvoxime.......	$C_{10}H_{14}.NOBz$........	−26.97	......	+26.47		

is always a mixture of two distinct isomerides (a and β), one of which is more powerfully rotatory than the other; a separation can be effected by treating the mixture with cold ether or chloroform. In addition to the above 4 optically active nitrosochlorides, inactive modifications may be prepared by mixing equal weights of the d- and l-forms of the a- and β-nitrosochlorides.

By warming limonene nitrosochlorides in alcoholic solution with piperidine, aniline, benzylamine, etc., Wallach obtained a series of crystalline a- and β-nitrolamines the rotation and m. p. of which are shown in the table on page 173.

The various nitrolamines from dextro- and lævo-limonene unite to form inactive compounds, in a manner similar to the nitrosochlorides from the same sources. Thus when equal quantities of the a-dextro- and lævo-nitrolpiperidines, m. p. 94°, are dissolved in petroleum spirit and the solutions mixed, a sparingly soluble inactive nitrolpiperidine, m. p. 154°, is at once precipitated. A similar inactive compound, m. p. 152°, is obtained by mixing the solutions of the β-nitrolpiperidines.

It will be noticed that the racemic compounds differ very widely from the optically active isomerides from which they are prepared; it is therefore not surprising that the identity of racemic or dl-limonene with dipentene remained for a long time unrecognised.

Terpinolene, $C_{10}H_{16}$.

This terpene does not appear to exist in nature. It is produced together with terpinene by the action of sulphuric acid on pinene and on other substances of the terpene group. It closely resembles dipentene in its structural formula and in its general characters.

Terpinolene tetrabromide crystallises from ether in lustrous tablets, m. p. 116°, and changes on keeping to an opaque white mass, which begins to melt below 100°, evolving gas and yielding a green liquid.

Terpinene, $C_{10}H_{16}$.

Terpinene has been found in Ceylon oil of cardamoms (*Elettaria cardamomum*). It exists comparatively rarely in nature, but occurs as a frequent product of the action of acids on other terpenes and their derivatives. Thus it is formed by the action of sulphuric acid on pinene, phellandrene, dipentene, dipenteneglycol, and cineol.

For the preparation of terpinene, 2 litres of rectified oil of turpentine should be treated with 70 c.c. of strong sulphuric acid. The acid must be added gradually, in quantities of 5 c.c. at a time, so that the temperature may not rise above the point at which the flask can be conveniently handled. The mixture is agitated at frequent intervals for 6 or 8 hours and the product then neutralised by sodium hydroxide, and distilled in a current of steam. The distillate is fractionated, and the portion distilling at about 180°, which consists of terpinene, collected separately.

Terpinene is a mobile liquid having an odour like that of lemons. It readily undergoes oxidation with formation of a resinous product.

Terpinene forms compounds with bromine and the halogen acids which are liquid at the ordinary temperature. The hydrochloride solidifies when strongly cooled.

Terpinene nitrosite, $C_{10}H_{16}N_2O_3$, is obtained by the action of sodium nitrite and dilute acetic acid on terpinene. It crystallises from alcohol in white prisms which dissolve without change in strong acids, but are decomposed by boiling with an alkali. By adding ammonia to a hot alcoholic solution of the nitrosite, *terpinene nitrolamine* is obtained. This compound has probably the constitution $C_{10}H_{15}(O.NO):N.OH$. It is deposited from its hot aqueous solution in needles, m. p. 116° to 118°, and dissolves easily in alcohol and alkalies. From the ethereal solution of the nitrolamine, hydrochloric acid precipitates crystals containing $C_{10}H_{18}N_2O,HCl$.

Other amines act with terpinene nitrosite in a manner similar to ammonia, forming crystallisable nitrolamines.

Phellandrene, $C_{10}H_{16}$.

Until recently, phellandrene was thought to exist only in optically isomeric (dextro and lævo) modifications. Recently, however, the existence of structural isomerides, known as α- and β-phellandrene, has been recognised and to these the structural formulæ shown on p. 171 have been assigned (Semmler, *Ber.*, 1903, **36**, 1749; Wallach, *Ann.*, 1904, **336**, 9; 1905, **340**, 1). *α-Phellandrene* exists in a dextrorotatory form, $[\alpha]_D + 17.6°$, in the oils of elemi and bitter fennel, and in a lævorotatory form in eucalyptus oil. It boils at 61° under 11 mm. pressure, has sp. gr. 0.844 at 19°, n_D 1.4732. Phellandrene is one of the most easily altered of the terpenes. It is radically changed by contact with acids, and is largely converted into terpinene by the action of hot alcoholic sulphuric acid.

The compounds of phellandrene with the halogens and halogen acids are not very characteristic. The *bromide* is a heavy oil which is converted into dipentene by heating with acetic acid and sodium acetate.

The most characteristic derivative is the *nitrosite*, $C_{10}H_{16}(NO)NO_2$, prepared by agitating the hydrocarbon with sodium nitrite and dilute acetic acid. Wallach describes the following process for its preparation: Phellandrene is diluted with petroleum and treated with dilute sulphuric acid in a beaker surrounded with a freezing mixture. A solution of sodium nitrite is then run in gradually, care being taken not to allow the temperature to rise above 4°.

Two modifications are produced, which may be separated by recrystallising from acetone and alcohol: *α-phellandrene* α-*nitrosite*, m. p. 112° to 113°, has $[\alpha]_D$ — 138°; *α-phellandrene* β-*nitrosite*, m. p. 105°, has $[\alpha]^D$ ± 40 to 46°; they have similar chemical properties and are perhaps stereoisomers.

β-Phellandrene, b. p. 57° under 11 mm. pressure, has sp. gr. 0.8520, n_D 1.4788 at 20°, and $[\alpha]_D$ + 18.54°; only the dextrorotatory form is known, as a constituent of water-fennel oil. *β-Phellandrene* α-*nitrosite*, m. p. 102° has $[\alpha_D$ — 159.30°; *β-phellandrene* β-*nitrosite*, m. p. 97o to 98°, shows no optical activity.

Sylvestrene, $C_{10}H_{16}$.

Sylvestrene occurs in Swedish and Russian turpentine oils together with dextro-pinene and hydrocarbons of higher b. p.[1] It is a liquid having an odour like that of fresh pine-wood.

Sylvestrene is one of the most stable of the terpenes, retaining its optical activity at 250° and undergoing little change by the action of alcoholic sulphuric acid. It combines with 2 molecules of hydrogen chloride, bromide and iodide, yielding compounds which melt, respectively, at 72°, 72°, and 66°. From the crystalline dihydrochloride, sylvestrene may be recovered unchanged by boiling with aniline. *Sylvestrene tetrabromide* forms monoclinic tablets, m. p. 135°. The *nitrosochloride* is very soluble in chloroform, and strongly dextrorotatory.

A fine blue colouration is produced on adding a drop of strong

[1] Swedish turpentine oil is obtained from the *tar* resulting from the dry distillation of the roots and stumps of pines, whereas American turpentine oil is made from the resinous exudation of the same species of pine. This difference in origin may account for the absence of sylvestrene from the American oil.

sulphuric acid to a solution of sylvestrene in acetic anhydride; this property is not shared by any other terpene.

The inactive racemic form of sylvestrene was prepared by Baeyer (*Ber.*, 1894, **27**, 1915, 3485; 1896, **29**, 2796) and was described by the name "*carvestrene.*"

Terpenes, $C_{10}H_{16}$. c. Dicyclic Terpenes.

Pinene, $C_{10}H_{16}$.

Pinene forms the most important constituent of French and American oils of turpentine. As prepared from the former source, it was called by Berthelot *terebentene*, and this name may be conveniently employed to designate the pinene of French turpentine oil. This variety of pinene is lævorotatory, while the pinene from American oil usually exhibits dextrorotation, though lævorotatory specimens have been obtained. This difference in optical properties extends to the various compounds and polymers of the pinenes from French and American turpentine oils.

Lævo-pinene, as obtained by a long series of fractional distillations from French turpentine oil, is a colourless mobile liquid of marked and characteristic odour. It has a sp. gr. of 0.8767 at 0°/0° and 0.8619 at 17.9°/17.9° (Riban), b. p. 156.5°, and gives $[a]_D - 40.3°$.
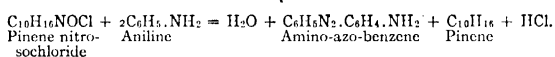
In addition to forming the main portion of French oil of turpentine, *lævo-pinene* occurs in the oils from *Pinus picea* and *P. sylvestris*, together with lævo-limonene and dipentene; in oil of olibanum, with a little dipentene and an unknown oxygenated compound, and in oil of rosemary to the extent of 80%, together with cineol, dextro- and lævo-borneol, and dextro- and lævo-camphor. The oils of thyme, sage, and anise also contain lævo-pinene.

Dextro-pinene, which forms the leading constituent of American turpentine oil, has the same sp. gr, b. p., and chemical characters as the pinene from the French oil, differing from the latter substance solely in the direction of its optical rotation.

Besides forming the greater part of American oil of turpentine, together with variable proportions of lævo-pinene and some dipentene, dextro-pinene also occurs, together with a sesquiterpene, in oil of galbanum; and, in association with an unknown oxygenated body, in the oil from *Daucus carota*.

Eucalyptene, laurene, massoyene, and olibene are mixtures of terpenes containing more or less pinene. Pinene also forms a notable proportion of the oils from the Guayana laurel, mace, sweet flag, cheken leaves, and bay leaves, and exists in smaller proportions in a great number of essential oils, including those from the juniper berry, Russian turpentine, *Pinus pumilio*, laurel, massoy, citron, fennel, myrtle, sage, valerian, hazel-wort, and eucalyptus.

It is very difficult if not impossible to obtain perfectly pure pinene from natural essential oils. A chemically pure substance closely resembling the natural pinenes, but optically inactive, is obtained by heating pinene nitroso-chloride with aniline:

$C_{10}H_{16}NOCl + 2C_6H_5.NH_2 = H_2O + C_6H_5N_2.C_6H_4.NH_2 + C_{10}H_{16} + HCl.$
Pinene nitro-   Aniline   Amino-azo-benzene   Pinene
sochloride

Pinene is nearly insoluble in water and aqueous liquids, but dissolves with facility in strong alcohol, and is miscible in all proportions with ether, chloroform, carbon disulphide, hydrocarbons, and fixed oils.

Pinene distils unchanged at 155° to 156° under the ordinary atmospheric pressure, and is readily volatile in a current of open steam. When heated in a sealed tube for several hours to about 300°, pinene yields a product formerly called *iso-terebentene*, which is so oxidisable that it is converted into a viscid mass on exposure to the air for a few hours. Iso-terebentene consists largely of dipentene, together with terpinene, terpinolene, and polymers of pinene. When the vapour of pinene or ordinary turpentine oil is passed through an iron tube heated to dull redness, a portion suffers conversion into the *isomers* dipentene, terpinene, and terpinolene; a second part is polymerised to "*colophene*"; a third suffers decomposition into hydrogen and *cymene*, $C_{10}H_{14}$; while a fourth portion splits up into 2 molecules of *isoprene*, C_5H_8 (W. A. Tilden). A notable amount of *meta-xylene* is also formed.

On treatment with a *small* proportion of sulphuric acid, pinene yields an optically inactive liquid which is a complex mixture of dipentene with variable proportions of terpinene, terpinolene, cymene, colophene, and a mixture of semi-solid products of high b. p. The more volatile portions of the product constitute the article commercially known as "*terebene*" (which see).

By treatment with concentrated sulphuric acid *in excess*, pinene is converted into *diterpene* or *colophene*, $C_{20}H_{32}$, with great rise of tem-

perature, some cymene being also formed. Colophene is also produced
by treating pinene or turpentine oil with a very small proportion of
boron fluoride, and still more highly condensed polymers can be
obtained by the action of antimonious chloride.

The action of air and other oxidising agents on pinene is described
under "Turpentine Oil".

Pinene is an unsaturated compound, and combines with the halogens,
hydracids, nitrosyl chloride, etc., to form definite additive compounds.
The combination is, however, attended with intramolecular change,
and hence unaltered pinene cannot, except in the case of the nitroso-
chloride, be regenerated from the compounds formed.

Pinene Hydrochloride. iso-Bornyl Chloride, $C_{10}H_{17}Cl$.—When
dry hydrogen chloride gas is passed into cold, dry pinene or tur-
pentine oil, the gas is rapidly absorbed with formation of a crystalline
substance which may be separated by pressure and purified by re-
crystallisation from alcohol or ether. The product is commonly
called *pinene hydrochloride*, but its formation is attended with in-
ternal molecular change and it is not possible to regenerate pinene
from it. The hydrochloride crystallises from alcohol or benzene in
white feathery needles. It closely resembles common camphor in
appearance, odour, and the property of subliming readily at ordi-
nary temperatures and has therefore sometimes been called by the
name of "artificial camphor," and is stated to have been used to
adulterate true camphor. Lævo-pinene hydrochloride from French
turpentine oil has a specific rotation of—32.2°, but that from the
American oil is more or less dextrorotatory. In either case the com-
pound melts at 131° (J. H. Long and Riban) or, according to Wal-
lach, at 125°, and boils at about 210° with only slight decomposition.

The chloride is insoluble in water. It dissolves in alcohol, but the
solution gives no precipitate with silver nitrate. Pinone hydrochlo-
ride is unaffected by alkalies at the ordinary temperature, but when
heated under pressure with alcoholic potassium hydroxide or dry
soap, or with an alcoholic solution of sodium acetate and sodium
hydroxide, it loses the elements of hydrogen chloride and yields *cam-
phene* (page 182).

When once formed, pinene hydrochloride is incapable of taking up a
second molecule of HCl, but if turpentine oil be left for some time in
contact with concentrated hydrochloric acid, or if a solution of pinene
or turpentine oil in ether, alcohol, or acetic acid be saturated with

hydrogen chloride gas, a compound containing $C_{10}H_{16}$, 2HCl is formed. This substance, however, is not a pinene compound, but consists of *dipentene dihydrochloride* (page 173).

Pinene-nitrosochloride, $C_{10}H_{16}$.NOCl, prepared by the action of a mixture of acetic and hydrochloric acids on a mixture of pinene with amyl and nitrite acetic acid, melts at 102–103° and is optically inactive. The *nitrosobromide* melts at 91–92°. *Nitrosopinene,* $C_{10}H_{15}NO$, prepared by reducing the nitrosochloride with alcohol and sodium, melts at 132°; it is reduced by zinc dust and acetic acid to *pinylamine,* $C_{10}H_{15}$-NH$_2$, and is oxidised by nitrous acid to *nitropinene,* $C_{10}H_{15}$.NO$_2$. By the action of potassium cyanide the nitrosochloride is converted into an *iso-nitroso-cyanide,* m. p. 171°, from which a series of derivatives may be prepared (Tilden and Burrows, Trans. Chem. Soc., 1905, **87,** 344). A series of compounds may also be obtained by the action of bases on the nitrosochloride, *e. g.,* the *nitrosobenzylamine,* $C_{10}N_{14}NO$-NH.C$_7$H$_7$, m. p. 122–123°. All the above compounds are inactive.

Camphene, $C_{10}H_{16}$.

Camphene is found only rarely in nature,[1] but it is of importance from its relation to pinene, borneol, and camphor. It occurs among the products of the action of concentrated sulphuric acid on turpentine oil, and is an important constituent of the so-called "terebene."

Pure camphene may be prepared from pinene hydrochloride (page 181) by heating it with potassium stearate or dry soap to 200° or 220°. It is also readily obtained by heating equal weights of the hydrochloride and anhydrous sodium acetate to 200° for several hours, with twice their weight of glacial acetic acid; or by simply boiling a mixture of pinene hydrobromide and glacial acetic acid under a reflux condenser.

Camphene may also be prepared by warming bornyl chloride, $C_{10}H_{17}Cl$, with an equal weight of aniline, and then heating the mixture to about 180°. The formation of aniline hydrochloride occurs suddenly, and the action is complete in a few minutes. When cold, the product is treated with hydrochloric acid, and the camphene distilled off in a current of steam. Camphene is also produced when *bornylamine,* $C_{10}H_{17}NH_2$ is heated with acetic anhydride. Ammonia is split off in the action, leaving camphene.

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[1] According to Bruhl, a camphene is probably present in the oils of myrtle and rosemary. E. J. Parry states that camphene occurs to a small extent in citronella, ginger, and camphor oils.

When prepared from pinene hydrochloride or hydrobromide, the
camphene obtained exhibits an optical rotation of the same kind as
that of the original pinene, but the product from bornyl chloride is
optically inactive.

Camphene is a white solid resembling camphor or paraffin-wax.
It has a peculiar odour suggesting that of camphor. The sp. gr. of
camphene in the solid state is about 0.860. It melts at 51°, and
boils at 160°. It is insoluble in water, but dissolves in alcohol,
ether, and benzene and crystallises from its concentrated alcoholic
solution in feathery leaflets.

Camphene readily unites with hydrochloric acid to form a cam-
phoroid body, m. p. 157°, which is probably identical with *bornyl
chloride*. The product differs from pinene hydrochloride by dissociat-
ing into camphene and hydrochloric acid by distillation, or more
gradually by mere contact with water.

In contact with bromine, camphene is gradually converted into the
substitution-product $C_{10}H_{15}Br$. It is generally stated not to form
an addition-product with bromine, but, according to Reychler, a *cam-
phene dibromide* can be obtained in prisms exhibiting double refraction
and melting at 90°.

By treatment with oxidising agents, such as chromic acid mixture,
camphene is converted into *camphor*, $C_{10}H_{16}O$, which exhibits an
optical activity of the same kind as that of the camphene from which
it was derived.

Bornylene, $C_{10}H_{16}$.

A terpene very closely related to camphene was obtained in admixture
with camphene, when bornyl iodide was heated to 170° in an auto-
clave with strong alcoholic potassium hydroxide. The bornylene
thus produced melts at 98°, and boils at 150° (Wagner and Brykner,
Ber., 1900, **33,** 2121). Bornylene and camphene are the only ter-
penes which are solid at ordinary temperatures.

Fenchene, $C_{10}H_{16}$.

Fenchene does not appear to occur naturally. It is formed by
the reduction of *fenchone*, $C_{10}H_{16}O$, the camphor of fennel oil, to which
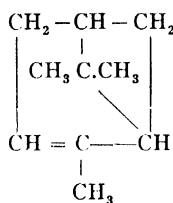fenchene bears the same relation that camphene does to laurel-camphor.

The fenchone is first reduced to *fenchyl alcohol*, $C_{16}H_{17}.OH$, which is then converted into the hydrochloride, and this body on heating .vith aniline yields fenchene. Fenchene also results when fenchyl alcohol is strongly heated with acid potassium sulphate. Fenchene forms a liquid monohydrochloride and an oily dibromide which has not been obtained pure. Fenchene resists the action of nitric acid to a remarkable extent. Wallach's researches have shown that fenchene is probably a mixture of two or more isomeric modifications.
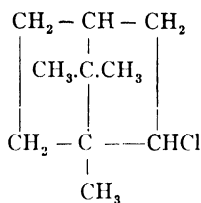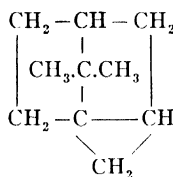
Thujene, $C_{10}H_{16}$.

This terpene is not known to occur in nature, but may be obtained by the dry distillation of the hydrochloride of thujylamine, a base prepared from thujene, one of the constituents of oil of thuja. Thujene has a sp. gr. of about 0.838 and b. p. 170 to 172°. Its molecule appears to contain 2 ethylenic bonds.

Thujene is distinguished from other terpenes by yielding an intense red coloration when its solution in acetic anhydride is treated with a drop of sulphuric acid.
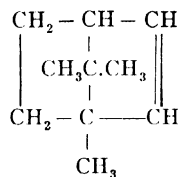
Constitution of the Dicyclic Terpenes.—The structural formulæ of the dicyclic ketones are less clearly established than those of the monocyclic compounds, and, although the synthesis of camphor, $C_{10}H_{16}O$, has been accomplished, nothing of the sort has been done in the case of the dicyclic terpenes, $C_{10}H_{16}$, except in so far as these may be derived from camphor. The following formulæ are generally accepted for pinene and its hydrochloride and for bornylene, but no general agreement has been arrived at in reference to the formula of camphene; the formulæ of fenchene and thujene are even less certainly established. It should be noted that the formula shown for pinene hydrochloride is capable of existing in 4 modifications corresponding with *d*- and *l*-borneol and *d*- and *l-iso*-borneol, the existence of which is well established. The existence of these isomeric chlorides has been one of the chief difficulties in establishing the constitution and identity of various preparations having the formula $C_{10}H_{17}Cl$; *e. g.*, pinene hydrochloride probably consists mainly of *d-iso*-bornylchloride, but mixed with *d*-bornylchloride.

$$CH_2 - CH - CH_2$$
$$CH_3 \; C.CH_3$$
$$CH = C \text{----} CH$$
$$CH_3$$

Pinene

$$CH_2 - CH - CH_2$$
$$CH_3.C.CH_3$$
$$CH_2 - C \text{----} CHCl$$
$$CH_3$$

Pinene hydrochloride
(Bornyl or *iso*-bornylchloride)

$$CH_2 - CH - CH_2$$
$$CH_3.C.CH_3$$
$$CH_2 - C \text{----} CH$$
$$CH_2$$

Camphene (?)

$$CH_2 - CH - CH$$
$$CH_3C.CH_3$$
$$CH_2 - C \text{----} CH$$
$$CH_3$$

Bornylene

Sesquiterpenes, $C_{15}H_{24}$.

The hydrocarbons of this formula, formerly called *cedrenes*, are closely allied to the true terpenes, and have often been confounded with them. They differ, however, from the terpenes in the following important respects: They are viscous, instead of being limpid; have a comparatively high sp. gr. (0.900 to 0.935 at 20°); boil at a high temperature (258° to 275°); form no crystalline hydrate similar to terpin (except caryophyllene); do not respond to Riban s test; are not distinctly polymerised by sulphuric acid; and do not yield hydrogen peroxide by treatment with air and warm water.

When the sesquiterpenes are treated with bromine or iodine and the product distilled with water, *cymene* is produced, just as when terpenes are similarly treated.

The essential oils of allspice, ginger, cedar-wood, cubebs, hops, rosewood, calamus, Indian hemp, cascarilla, and patchouli consist chiefly or largely of sesquiterpenes. Oil of cloves rarely contains more than 20% of sesquiterpene, and often not more than 10%.

A considerable number of sesquiterpenes have been described, but the distinct individuality of the great majority is highly questionable. The following are the best defined members of the class:

Sesquiterpene	Chief sources	Sp. gr.	B. p.	$[\alpha]_D$	Other characters
Cadinene....	Oils of cade, galbanum, patchouli, etc.	0.918 at 20°	274° to 275°	--98.6	....
Caryophyllene	Oils of clove, copaiba, etc.	0.908 at 15°	258° to 260° 123.4° at 13 mm.	--9°	Forms a crystalline alcohol melting at 96°. Refractive index, 1.50094.
Clovene.....	Isomerisation of caryophyllene	0.930 at 18°	261° to 263°	α_D --35.39°	Does not form a crystalline alcohol. Refractive index, 1.50066.
Cedrene	Oil of cedarwood	0.936 at 15°	262° to 263°	--60°	According to Rousset $[\alpha]_D = -47.9°$.
Humulene....	Oil of hops	0.900 at 20°	263° to 266° 132.7° at 13 mm.	--10.8°	Forms liquid tetrabromide and dihydrochloride.
Patchoulene.	Action of dehydrating agents on patchouli alcohol	0.939 at 23°	254° to 256°	....	Refractive index, 1.50094.
Zingiberene..	Oil of ginger	0.872 at 15°	269° to 270° 134° at 14 mm.	--69° to --73.5°	Refractive index, 1.49399. Forms liquid tetrabromide.
Cannibene....	Oil of Indian hemp	0.897 at 15°	258° to 259°	--8.6°	....

In addition to the above, cubeb oil and betel-leaf oil contain the sesquiterpene *cubebene*, having a sp. gr. of 0.917 at 15° and boiling at 260°. Cubeb oil is said to contain a second sesquiterpene with a slightly different b. p., and pure cubebene is not improbably identical with cadinene.

The sesquiterpenes are characterized by the formation of dihydrochlorides and tetrabromides; they are therefore doubly unsaturated. They form crystalline nitrosochlorides (NOCl), nitrosates ($+N_2O_4$), and nitrosites ($+N_2O_3$). The m. p. of the chief derivatives are shown in the following table:

	Caryophyllene	Humulene	Cadinene	Zingiberene
Dihydrochloride......	69 to 70°	liquid	117 to 118°	168 to 169°
Nitrosochloride.......	158	164 to 167°	93 to 94°	96 to 97°
Nitrosate......... ...	147 to 150°	162 to 163°	105 to 110°	86 to 88°
Nitrosite..............	α 113-114°; β 146-148°	α 127°; β 172°	....	....
Isonitrosite	53 to 56°	165 to 168°	....	....
Nitrol-benzylamine....	α 167, β 128	136°	....	....
Nitrol-piperidine......	141 to 142°	153°	....	....

Diterpenes and Polyterpenes.

These hydrocarbons are formed by the action of heat or poly-merising agents on isoprene and the terpenes. They are not further polymerised by sulphuric acid, and combine with smaller proportions of hydrochloric acid than the unpolymerised terpenes. Their chemical characters have been little studied.

Colophene, $C_{20}H_{32}$, or $(C_5H_8)_4$, is produced in considerable quantity when turpentine oil is agitated with strong sulphuric acid or phosphoric anhydride, and is present in rosin oil. It is a very viscid liquid of 0.939 sp. gr., which begins to boil at about 318°, and exhibits a strong blue fluorescence. It forms an unstable hydrochloride. Antimony trichloride converts turpentine oil into a colophene from which absolute alcohol extracts a liquid, leaving solid *tetraterebenthene*, $C_{40}H_{64}$ as an amorphous mass, soluble in ether, carbon disulphide, benzene, or turpentine, and melting above 100°. It is converted into liquid colophene by distillation.

The oils of black pepper, copaiba, and gurjun balsam contain a diterpene, or mixture of that nature, b. p. 250° to 260°. The compound has not been obtained in a state of purity.

Diterpilene, isomeric with colophene, is produced when oil of turpentine is heated with absolute formic acid. It is a thick oily liquid, optically inactive and smelling like copaiba balsam. It has a sp. gr. of 0.9404 at 0°, and resinifies on exposure to air.

KETONES OF ESSENTIAL OILS.

By T. MARTIN LOWRY, D. Sc., A. C. G. I.

Compounds of ketonic functions occur in essential oils more commonly than was recognised till recently. They may be divided into two groups—open-chain compounds, such as methyl-heptyl and methyl-nonyl ketones; and cyclic ketones, such as camphor, fenchone, and carvone.

Open-chain Ketones.—In accordance with a general reaction, aldehydes and methyl-ketones may be isolated from essential oils by the action of sodium hydrogen sulphite. This separation is usually made after removing the free acids by shaking with sodium carbonate, and the esters by hydrolysing with alkali hydroxide. For the purposes of the test the oil, or a suitable fraction of it, is shaken either alone or in an ethereal solution with a concentrated solution of sodium hydrogen sulphite. The crystalline compound $R_1R_2C(OH)SO_2$-ONa is washed with ether, drained, pressed, and decomposed with sodium hydroxide either alone or in presence of ether, and the ketone is then separated and purified by the ordinary methods.

Methyl-nonyl ketone, $CH_3.CO.C_9H_{19}$, forms the major constituent of European oil of rue, of which it constitutes nearly 90%. Thoms (*Ber. deut. pharm. Ges.*, 1901, **10**, 3) has shown that it is associated with about 5% of the heptyl ketone (*vide infra*). The Algerian oil contains about 90% of these ketones, but in this case there is nearly twice as much of the lower as of the higher homologue. Power and Lees (Trans., 1902, **81**, 1585) found 80% of the two ketones in an oil apparently of Algerian origin.

The ketone boils at 232° under 760 m.m. pressure and has a sp. gr. 0.8263 at 20.5°/16° (Power and Lees, p. 1589). The oxime, $C_9H_{11}C(CH_3):NOH$, melts at 46° and the *semicarbazone*, $C_9H_{11}C(CH_3)$: $N.NH.CO.NH_2$, at 122°. The enolic *benzoyl-derivative*, $C_8H_{17}CH$: $C(CH_3).O.CO.C_6H_5$, prepared by boiling the ketone with benzoyl chloride and distilling under reduced pressure, b. p. 233 to 235° under

50 m.m. pressure, is immediately hydrolysed by warm dilute alcoholic potassium hydroxide (Lees, Trans., 1903, **83,** 149).

Methyl-n-heptyl ketone, $CH_3.CO.C_7H_{15}$, boils at 195° under 763 mm. pressure and has sp. gr. 0.8296 at 14°/16° (Power and Lees, p. 1588). The *semicarbazone* melts at 119° to 120°. The enolic *benzoyl derivative* boils at 210° to 211° under 50 mm. pressure. •˙

Methyl-heptenone, $CH_3.C(CH_3):CH.CH_2.CH_2.CO.CH_3$, an unsaturated open-chain ketone, is present to the extent of 1 to 4% in lemon-grass oil. For its extraction the fraction of the oil distilling at 180° should be agitated with a solution of sodium bisulphite in 1.5 parts of water. The ketone liberated from the solid bisulphite compound on treatment with sodium hydroxide is optically inactive, has n_D^{20} 1.43805, and yields a semicarbazone, m. p. 134°. Methyl-heptenone also results from the distillation of cineolic anhydride.

Irone, $C_{13}H_{20}O$, a cyclic methyl ketone of the formula

$$(CH_3)_2.C\begin{cases} CH(CH:CH.CO.CH_3).CH.CH_3 \\ \\ CH:CH \end{cases}CH_2,$$
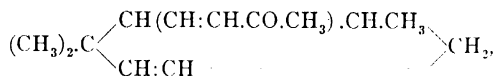
isomeric with the synthetic "ionones" prepared from citral, and, like them, possessing an odour of violets in alcoholic solution, is contained in dried orris root (iris root), from which Tiemann and Kruger extracted it in the form of an insoluble dextrorotatory oily substance of sp. gr. 0.939 at 20°, and b. p. 144° under 16 mm. pressure. Although the molecule contains a ring system, the ketonic group is present in a side chain, and the compound is therefore conveniently classified with the open-chain ketones.

Cyclic Ketones: General.

The cyclic ketones are for the most part closely related to the terpenes, and, like them, contain 10 carbon atoms in the molecule. That this relationship is fundamental and not merely superficial is shown by the fact that camphor is now prepared synthetically on a considerable scale from turpentine, and may in its turn be converted into camphene, another member of the terpene group. The cyclic ketones may be classified conveniently according to their composition into 4[1] groups:

a. Ketones $C_{10}H_{18}O$, containing a single ring; *e. g.*, menthone.

[1] The saturated open-chain ketone $C_{10}H_{20}O$ does not appear to be present in essential oils, although the C_9 and C_{11} ketones are both found in oil of rue.

*b*. Ketones $C_{10}H_{16}O$, containing a ring and a double bond or 2 double bonds; *e. g.*, camphor.

c. Ketones $C_{10}H_{14}O$, containing a ring and 2 double bonds, 2 rings and 1 double bond, or 3 rings.

d. Various ketones containing more (or less) than 10 carbon atoms, such as matico-camphor,$C_{12}H_{20}O$. These are conveniently described in conjunction with the ketones to which they are most closely related (see p. 210).

Cyclic Ketones, $C_{10}H_{18}O$.

Menthone, $\mathrm{CH.CH} \underset{\mathrm{CH_2-CO}}{\overset{\mathrm{CH_2-CH_2}}{<}} \mathrm{CH.CH.(CH_3)_2}$,
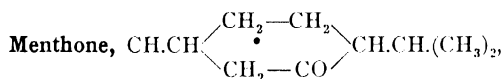
occurs with menthol in peppermint oil. It is a liquid with b. p. 207°, sp. gr. 0.896 at 20°; the natural ketone is dextrorotatory, but the lævo-isomeride can be prepared by oxidation of menthol. It gives an *oxime*, m. p. 58°, and a *nitroso* derivative, m. p. 112.5°.

Cyclic Ketones, $C_{10}H_{16}O$. Camphor, $C_8H_{14} \underset{\mathrm{CO.}}{\overset{\mathrm{CH_2}}{<}}$
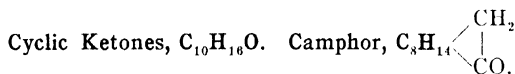
Origin.—Common or Japan camphor occurs in minute crystals in the wood of the camphor-laurel (*Laurus* or *Cinnamomum camphora*,) and is extracted by distilling the chopped-up branches of the tree with water.
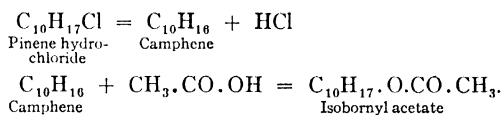
The crude camphor thus obtained is exported from Japan and Formosa, and to a limited extent from China, and is refined in Europe by mixing it with a small proportion of lime or charcoal and subliming it in large glass vessels called "bombolas," or by subliming it from iron retorts into a cooled chamber, where it condenses in the form of flowers of camphor. It is subsequently pressed into transparent cakes by hydraulic power. Camphor also occurs in the oils of sage, lavender, spike-lavender, and rosemary.

Preparation.—It can also be prepared by oxidising the secondary alcohol borneol, $C_{10}H_{18}O$, which is exported on a considerable scale from Borneo and Sumatra under the name of Borneo camphor. This method of preparation has acquired great importance in recent years as the last stage in the manufacture of camphor from turpentine.

Artificial Camphor.—The first stage in the process consists in

passing dry hydrogen chloride into well-cooled and carefully dried turpentine, when pinene hydrochloride, $C_{10}H_{17}Cl$, is thrown down as a white crystalline mass. The hydrochloride resembles camphor somewhat closely, and is sometimes sold under the misleading title of artificial camphor. It can, however, be readily distinguished by using the ordinary tests for halogens; thus, if a copper wire be heated in the flame of a Bunsen burner until it no longer produces a colouration, an intense green tint is developed by dipping the wire into the fictitious "camphor" and again heating it in the flame; no such colouration is produced by natural camphor, nor by genuine camphor prepared artificially from turpentine as described below if the later steps in the manufacture have been efficiently carried out.

The second stage in the preparation of artificial camphor consists in the removal of hydrochloric acid from the pinene hydrochloride, and the production of iso-bornyl acetate either directly in one process or indirectly with separation of camphene as an intermediate product. In the latter case the removal of the hydrogen chloride is effected by means of (a) ammonia or organic bases or (b) alkalies in the free state, or in combination with a weak acid, as in the form of soap; the camphene is then converted into *iso-bornyl* acetate by heating with glacial acetic acid *plus* about 5% of sulphuric acid.

$$C_{10}H_{17}Cl = C_{10}H_{16} + HCl$$
Pinene hydro-   Camphene
chloride

$$C_{10}H_{16} + CH_3.CO.OH = C_{10}H_{17}.O.CO.CH_3.$$
Camphene   Isobornyl acetate

A direct conversion into the acetate can be effected by heating the hydrochloride with glacial acetic acid *plus* 5 to 10% of zinc chloride (Weizmann, B. A. Report, Dublin, 1908, p. 661). The acetate is hydrolysed by boiling with alcoholic sodium hydroxide, the alcohol distilled off, and the borneol, which separates in white crystals is oxidised by means of (e. g.) nitric or chromic acid to camphor. It is important that no unchanged hydrochloride should be left in the finished product, as a small proportion of chlorine is sufficient to render the material useless for the manufacture of celluloid, and undesirable for many other purposes. When properly prepared, however, artificial camphor resembles the natural product in all its essential properties and differs from it only in the absence of optical activity.

Physical Properties.—Camphor is known commercially in two forms—as "flowers" of camphor, in the form of small crystals obtained by subliming the camphor in a chamber; and in semi-transparent blocks, prepared from the flowers by compression. By slow sublimation at atmospheric temperatures it is obtained in brilliant crystals belonging to the hexagonal system. Such crystals are often found deposited on the sides of the bottles in which it is preserved. It vaporises readily, when exposed to the air, and sublimes without residue when heated. When partially enclosed so as to check the rapidity of vaporisation, it melts at 175° and boils without decomposition at 204°. It is readily inflammable and burns with a smoky flame.

Camphor is somewhat lighter than water, the sp. gr. being given variously from 0.980 to 0.996. When thrown on the surface of clean water, camphor goes through rapid whirling movements, which are arrested by the addition of a drop of oil.

Its solubility in water is very slight, amounting to only about 1 part in 1,000, but it is freely soluble in all organic liquids. It dissolves in less than its own weight of alcohol (120:100) of 0.806 sp. gr., and is readily soluble in ether, chloroform, acetone, glacial acetic acid, carbon disulphide, and fixed oils. A saturated solution of camphor in olive oil contains 27% by weight of camphor. Its solubility in water is only slightly affected by the addition of small amounts of acid or alkali, but it dissolves readily in concentrated hydrochloric, hydrobromic, and sulphuric acids. The solid camphor possesses the property of absorbing gaseous hydrogen chloride, nitrogen peroxide, and sulphur dioxide, forming liquids which are decomposed by the addition of water. The compound of camphor with sulphur dioxide has been proposed as a disinfectant under the name of "Thiocamph." Camphor also liquefies when triturated or heated with menthol, thymol, phenol or chloral hydrate; the products, which appear to be definite compounds, have received a limited application in medicine.

Ordinary camphor is dextrorotatory.

The essential oil obtained by distillation from the leaves of fever-few (*Matricaria parthenium*) contains a variety of camphor agreeing in all respects with that obtained from the camphor-tree except that it exhibits a left-handed rotation equal to the dextrorotation of the latter kind. By mixing these two varieties of camphor in equal proportions, a *racemic camphor* is obtained which is optically inactive

and is apparently identical with the camphor prepared from tur-
pentine. This inactive camphor has m. p. 179°, and yields derivatives
which differ in their solubilities and m. p. from the parallel products
obtained from ordinary camphor. (See A. Haller, *Compt. rend.*,
1887, **105**, 66.) A camphor which appears to differ from laurel-
camphor merely in being optically inactive is contained·in the fraction
of oil of sage distilling between 205° and 208°.

The sp. rot. of camphor varies considerably with the nature of the
solvent and the concentration of the solution. Landolt gives the
formula

$$[\alpha]_D = +\overline{5}5.4 - a.q,$$

where q is the number of grm. of solvent in 100 grm. of the solution.
The value of a varies with the solvent, being 0.1372 for alcohol and
0.1632 for benzene. Thus the apparent sp. rot. power of a solution
of 10 grm. of camphor in 90 grm. of alcohol will be:

$$55.4° - 12.3° = +43.1°$$

From the observations of Partheil and van Haaren (*J. Soc. Chem. Ind.*,
1900, **19**, 684) it appears that the more dilute the alcohol, the lower the
apparent sp. rot. of the dissolved camphor. Hence the amount of the
latter cannot be accurately deduced from the observed rotation, unless
the strength of the alcohol be also known. Further, when the solvent
is kept of constant strength the sp. rot. decreases slightly as the % of
camphor increases. Partheil and van Haaren propose the formula:
$P = 1.5152\ a$, where P is the percentage of camphor by weight and a
the observed rotation for 200 mm. To ascertain the sp. gr. of the
alcohol used (S), they propose the following formula:

$$S = \dfrac{100 - p}{\dfrac{100}{d} - 1.05\,p}\ ;\ \text{where } p \text{ is the % of camphor by weight and } d \text{ the}$$

sp. gr. of the camphorated spirit. Partheil and van Haaren give the
following table:

No.	Sp. gr. of alcohol used	Camphor, %	Observed rotation, 200 mm.	Sp. rot., $[a]_D$
1	0.7896	10	6.98°	43.4362
2	0.8212	10	6.78°	40.6666
3	0.8505	10	6.69°	39.0439
4	0.8637	10	6.65°	38.1439
5	0.8781	10	6.60°	37.2755
6	0.8909	10	6.59°	36.7622
7	0.9007	10	6.59°	36.4008
1	0.7895	8.37	5.79°	43.2142
2	0.7895	6.81	4.69°	43.1411
3	0.9007	8.35	5.48°	36.2929
4	0.9007	6.82	4.40°	35.6951

The following determinations of the sp. rot. of camphor when dissolved in fixed oils are by P. Chabot (*Compt. rend.*, 1890, **3**, 231):

	Olive oil	Almond oil	Grape-seed oil
$[a]_D$ in 3% solution	55.7°	56.8°	54.4°
$[a]_D$ in 20% solution	55.2°	54.3°	54.3°

From these results it appears that the value of $[a]_D$ varies little, but somewhat increases, with the dilution, whereas the reverse is the case with solutions of camphor in alcohol and benzene. (See also Leonard and Smith, page 198.)

Physiological Properties.—Camphor has a peculiar fragrant odour and somewhat bitter, burning taste, followed by a sensation of cold. It has distinct, but not very powerful, antiseptic properties, and is inimical to insect life. Hence its employment for preserving animal specimens in museums, etc.

It is extensively employed in medicine, both internally and externally. In large doses it is distinctly poisonous, the most marked symptoms being cardiac depression, lividity of countenance, convulsions, stupor, retention of urine, and, in extreme cases, collapse. When ingested by the dog, camphor appears in the urine as *campho-glycuronic acid*, $C_{16}H_{24}O_8$, which when boiled with dilute hydrochloric acid yields *camphoral*, $C_{10}H_{16}O_2$, a substance which crystallises in thin tablets,

m. p. 197° to 198°, sublimes readily, and yields camphoric acid on oxidation.

The three chief pharmaceutical preparations of camphor are as follows:

Camphor water, B. P. (1898), is a 0.1% solution of camphor, and is directed to be prepared by dissolving 1 part by weight of camphor in sufficient alcohol (90%) to form 3 volumes, and then pouring the solution gradually with shaking into 1000 parts of water, the liquid being occasionally shaken until the camphor is dissolved. The solution has an extensive use in medicine. The United States Pharmacopœia (8th Rev., 1900) preparation is apparently stronger, as it is made by rubbing up 8 grm. of camphor in 8 c.c. of alcohol with 15 grm. of purified talc; and after most of the alcohol has evaporated spontaneously distilled water is gradually added. The total volume is 1,000 c.c. The mixture is filtered on a well-wetted filter.

Spirit of Camphor, B. P. (1898), is a solution of 1 part of camphor in 9 of 90% alcohol. The corresponding preparation of the United States Pharmacopœia (8th Rev.) is made by dissolving 100 grm. of camphor in sufficient alcohol to form 1,000 c.c. Such a solution occupies fully the volume of the spirit used *plus* that of the camphor before solution, there being slight expansion rather than contraction in the process of solution. Rubini's "Essence of Camphor" (*Spiritus camphoræ fortior*) is a solution of camphor in an equal weight of rectified spirit.

On diluting an alcoholic solution of camphor with water, the solid is precipitated in white flocks. If the proportion of alcohol exceeds a certain limit, no amount of dilution will effect precipitation of the camphor.

Liniment of Camphor or Camphorated Oil, B. P. (1898), is a solution of 1 part by weight of camphor (in flowers) in 4 parts by volume of olive oil. Hence the preparation, when properly made, contains almost exactly 21% by weight of camphor. The corresponding preparation of the United States Pharmacopœia is a solution of 1 part of camphor in 4 of cottonseed oil.[1]

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[1] Numerous samples of "camphorated oil" purchased in the West Riding of Yorkshire under the provisions of the Sale of Food and Drugs Act, were found to contain various proportions of camphor from 21% down to less than 1%, from 3 to 5% being quite common. Cottonseed and sesame oils were in some cases substituted for olive oil, and the vegetable oils were not unfrequently partly or wholly replaced by heavy mineral oil. Methods for the detection of the various vegetable oils will be found in Vol. 2. There is no foundation for the statement frequently made in defense that the camphor readily volatilises from the solution.

In addition to the official preparations of camphor and the camphor derivatives, there are mixtures of camphor used in medicine (Coblentz, Newer Remedies, 4th ed., 1908, p. 29). Camphor, phenylated, is made by melting together equal parts of camphor and phenol. There are also compounds of a similar nature in which salicylic acid, resorcinol, thymol, etc., are melted with camphor.

In addition to its employment in medicine, camphor is used extensively for the manufacture of the nitrocellulose products known as *celluloid* and *xylonite*, and is or was an ingredient of some varieties of blasting gelatin and smokeless powder.

Crude camphor (according to S. S. Sadtler, private communication) is generally examined for dirt, water, and amount of oil; sometimes for the identity of the camphor itself.

.**Dirt** is estimated by evaporating 5 grm. in a warm place, such as over a steam-bath.

Water is estimated by distillation with water-saturated xylene (Marcusson method). The amount of water coming over with the xylene is measured in a suitable burette.

Essential oil can be estimated with a fair degree of accuracy by preparing some fine camphor by sublimation,[1] and making known mixtures with oil of camphor from which the camphor had been chilled and expressed.

As an example of a test of this nature carried out in Sadtler's laboratory, a sample of camphor melting at 160° was to be compared with known mixtures, and the following series of standards were made.

Oil, %	Camphor, %	M. p.
0	100	175
1	99	173
2	98	171
3	97	169
4	96	167.5
5	95	166
6	94	164.5
7	93	163
8	92	161.5
9	91	160

The sample in question was considered as having 9% of oil as its m. p. was 160°.

[1] Sadtler found it best to sublime it several times from an admixture of scale paraffin which held back traces of oil of camphor.

Estimation of Camphor.—Camphor can be readily separated from non-volatile substances by distilling the mixture in a current of steam, but its accurate estimation in presence of other volatile compounds presents some difficulty. The proportion of camphor present in camphor liniment and similar preparations can be ascertained with considerable accuracy by the direct observation of the optical activity of the liquid.

The following figures by N. Leonard and H. M. Smith (*Analyst*, 1900, **25,** 202) show the optical activity of solutions of various strengths of camphor in olive oil. Line 4 in the table shows the observed angular rotation of the solution in a 200 mm. tube. Line 5 shows the calculated angular rotation for 1% of dissolved camphor. These latter figures are corrected for the small rotation of olive oil itself, which, according to Bishop (*J. Soc. Chem. Ind.*, 1887, **6,** 750), is $+0.13°$ for 200 mm. Line 6, which has been added by Allen, shows the apparent sp. rot. of camphor calculated from Leonard and Smith's data.

	A	B	C	D
1. Dissolved camphor, %	5.32	11.26	20.66	26.78
2. Sp. gr. at 60° F	0.91903	0.92173	0.92604	0.92911
3. Rise of sp. gr. for 1% camphor	0.000446	0.000450	0.000454	0.000465
4. Angular rotation per 200 mm	5.26°	11.35°	20.74°	26.79°
5. Angular rotation for 1% camphor	0.964°	0.998°	0.998°	0.996°
6. Apparent sp. rot. of dissolved camphor.	52.4°	54.0°	53.9°	53.6°

D was a saturated solution prepared by gently warming olive oil with excess of camphor, cooling to about 10° and filtering. The contained camphor was then ascertained from the loss of weight sustained on heating a portion of the solution at 110° to 120°.

It will be seen from these results that the rotation of the liquid is increased by nearly 1° for each unit % of camphor present, and that the observed angular rotation of a sample of camphorated oil in a 200 mm. tube gives at once, without calculation, the % of camphor with sufficient accuracy for most purposes. The rotation appears not to be appreciably influenced by ordinary variations of temperature.

Leonard and Smith found the rotation of two specimens of rape oil to be −0.16° and −0.3°, and of sesame oil +1.6°, per 200 mm., results which are in accord with those of Bishop, while two samples of fluorescent mineral oil gave them rotations of + 0.12° and + 0.42°. Experi-

ments with rape oil and mineral oil showed, however, that the increased rotation caused by the solution of camphor in these oils is practically the same as with olive oil, so that if the nature of the oil used in the preparation of the sample is known, the process is still applicable. For the identification of the oil used, they found that the sample could be examined directly with the refractometer, the refractive index of the oil being apparently almost unaffected by the presence of dissolved camphor.

For the gravimetric estimation of camphor in camphor liniment, 5 grm. of the sample should be heated in a shallow capsule to 120° for about 2 hours, when the loss of weight will be that of the camphor volatilised.[1] Or a good plan is to heat the liquid in a capsule over a water-bath, when the greater portion of the camphor will readily be volatilised and the remainder can be removed in the air-bath as before (Tankard). The same method will give fairly good results with samples containing heavy mineral oil, but in the case of a more volatile fraction of petroleum being present the loss of weight will, of course, not be due solely to the camphor. F. Foerster drives a current of open steam through the oil, and when the distillate amounts to about 300 c.c. redistils it with the addition of a little alkali and a spiral of platinum wire to prevent bumping. The distillate is agitated with benzene and the amount of camphor deduced from the optical activity of the liquid. (See page 194.)

F. Foerster (Ber., 1890, 23, 2981) employs a similar process for the estimation of the camphor in celluloid, xylonite, ivorine, and similar preparations. For this purpose, a quantity of the sample containing from 2 to 3 grm. of camphor is treated in a flask furnished with a condenser and tap-funnel with sufficient of a 10% solution of sodium hydroxide to saponify the substance. The flask is heated to about 80° till saponification is complete, when sufficient concentrated alkali is added to raise the strength of the liquid in the flask to about 10% of NaOH. The contents of the flask are then diluted, if necessary, to about 250 c.c., and distilled till about half the volume has passed over. The condenser should be connected air-tight upon the receiver, which

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[1] Some samples of olive oil appear to gain slightly in weight on heating, while others lose weight. (See A. W. Nunn, Pharm. Journ., 1902, 69, 106.) It has been proposed to make a correction for this change, but this refinement is unnecessary.

An indirect method of estimating camphor in the liniment (in the absence of mineral oil) consists in applying Kœttstorfer's saponification process. The weight of potassium hydroxide (KOH) required for the saponification, multiplied by 5, gives the weight of fatty oil present in the portion of the sample operated on. 5 grm. is a suitable quantity of oil to employ. The results are satisfactory.

should have a second orifice fitted with a **U**-tube containing an exact measure of benzene, to catch any uncondensed camphor-vapour.[1] When the distillation is complete, this benzene is added to the contents of the condenser, and more added to bring the total volume employed to 25 c.c. The contents of the receiver are then agitated to dissolve the camphor in the benzene, the latter separated from the water, brought to a temperature of 20°, and the optical activity observed with a polarimeter. According to Foerster, the specific rotation of camphor in benzene solution is $+39.755° + 0.17254\ t$, whence $[a]_D = +40.11°$ at 20°. (Compare Landolt's formula on page 194.)

From *alcohol*, camphor may be partially separated by addition of water (see above), the solution being afterward fractionally distilled. Or the camphor may be extracted from the largely diluted liquid by agitating it with a known weight or measure of a heavy petroleum fraction, and its amount deduced from the increased weight or volume of the separated solvent. O. Schmatolla agitates 10 grm. of the spirit in a burette with about 30 c.c. of a saturated solution of common salt, and dissolves the precipitated camphor by adding exactly 1 c.c. of a petroleum oil and gently rotating the burette. The increase of volume of the petroleum is noted, each 1.02 c.c. representing 1 grm. of camphor.

When the proportion of camphor in an alcoholic solution is roughly known, the amount may be deduced from the optical activity of the liquid, but the result will be only approximate unless the strength of the alcohol be also known. (See page 195.)

The following process is given by E. Deussen (*Arch. Pharm.*, 1909' **247,** 307) for the *estimation of camphor in spirits of camphor.* Five grm. of the spirit of camphor are weighed into a tared 50 c.c. Erlenmeyer flask and 20 grm. of cold saturated ammonium sulphate solution and 30 grm. of water added. After well shaking the mixture is set aside in an ice-chamber for 12 hours. The separated camphor is drained and aggregated into a ball by means of a nickel spatula. The filter is covered with a watch-glass and another small watch-glass and a piece of card about the size of a post-card are tared. The camphor is spread out thinly with the nickel spatula on a porous tile, covered for some minutes with a watch-glass, and then transferred as completely as possible to the tared card, covered with the tared watch-glass and weighed. The amount of camphor found

Foerster uses a special form of receiver.

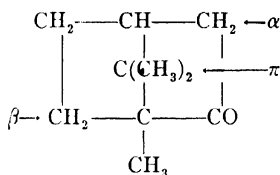by this process is within 4 to 6 per cent. of the actual amount present.

The following process is proposed by F. W. Richardson and W. Walton (*Analyst*, 1908, **33**, 463–466) for the analysis of camphorated oil in order to detect and estimate synthetic camphor, oil of turpentine, and essential oil of camphor, any or all of which may be present in addition to natural camphor. 10 c.c. of the camphorated oil are placed in a small retort, and heated to a temperature of 200° by means of an oil-bath; a current of dry carbon dioxide is passed through the retort during the heating, and the neck of the retort is connected with a weighed, two-necked Woulff's bottle. A weighed, small spiral glass condenser is fitted in the second hole of this bottle. The volatile sub-stances collecting in the neck of the retort, the Woulff's bottle, and condenser are weighed (the neck of the retort being cut off for this purpose), dissolved in carbon tetrachloride, and the solutions are united. This solution is weighed, and portions are used for the esti-mation of the sp. gr., iodine number, and polymerisation with sul-phuric acid. The last-mentioned process is carried out by treating a weighed portion of the solution (about 1/2) with 1/3 of its volume of sulphuric acid, sp. gr. 1.84, the acid being added slowly and the mix-ture cooled. The latter is then distilled in steam, and the carbon tetra-chloride solution separated from the distillate and weighed; the change in sp. gr. and ref. index of the solution enables the weight of the total camphors to be calculated, while the polarimetric reading in a 200 mm. tube, multiplied by 0.22385 and divided by 0.95, gives the amount of natural camphor. This deducted from the total camphors leaves the quantity of synthetic camphor. When the amounts of the two camphors are known, the iodine number due to turpentine and oil of camphor enables the % of the last-named substances to be cal-culated. The following iodine numbers are assumed in the calcula-tion: natural camphor, 5; synthetic camphor, 7; essential oil of cam-phor, 190; and oil of turpentine, 370.

Lohrmann (Ber. deutsch. Pharm. Ges., 1909, **19,** 222) discusses the points of difference by which natural, artificial, and synthetic camphors are distinguished. The optical rotation in alcoholic solu-tion is preferred as a means of estimating the amount of natural cam-phor in presence of synthetic camphor. The importance in the celluloid industry of having synthetic camphor free from chlorine is emphasized. Borneol and isoborneol are readily estimated in syn-

thetic camphor by the acetylation method.   The m. p. affords a use-
ful indication of the purity of synthetic camphor.   For celluloid
manufacture the camphor should be free from traces of acid and the
ash should in no case exceed o.02%.

Constitution and Synthesis of Camphor.

The formula for camphor proposed by Bredt in 1893,

$$
\begin{array}{c}
CH_2\text{---}CH\text{---}CH_2 \;-\alpha \\
| \qquad\quad | \qquad\quad | \\
\quad\quad C(CH_3)_2 \;\text{---}\pi \\
| \qquad\quad | \qquad\quad | \\
\beta-\,CH_2\text{---}C\text{---}CO \\
| \\
CH_3
\end{array}
$$

has been verified by Kommpa's recent synthesis (*Ber.*, 1901,
34, 2472; 1903, **36,** 4332).   It is therefore unnecessary to recite the
evidence previously adduced in favour of this and other formulæ.
The majority of the chemical reactions of camphor involve only the—
CH_2CO—group shown on the right-hand side of the formula, and the
abbreviated formula $C_8H_{14} \diagdown \begin{smallmatrix} CH_2 \\ | \\ CO \end{smallmatrix}$ is therefore frequently used to rep-
resent the ketone and its simpler derivatives.

Three types of substitution-derivatives are known in addition to
those involving the carbonyl group, viz.:

1. a-*Derivatives*, in which the hydrogen of the—CH_2CO—group is
displaced.   Owing to the lack of symmetry in the molecule, the
2 hydrogen atoms do not occupy equivalent positions, and 2 series
of stereoisomeric compounds may be prepared.   These are fre-
quently distinguished as α-and α'-derivatives, the α-position being
that occupied by the halogen, and the α'-position that occupied by
hydrogen in the common or α-bromocamphor.

2. β-*Derivatives*, in which a hydrogen atom is displaced from the
methylene group which occupies a position in the molecule symmetric-
ally situated with reference to the carbonyl group.   These may be
prepared by sulphonation (Reychler, Armstrong, and Lowry), by
bromination in presence of hydrobromic acid, and indirectly through
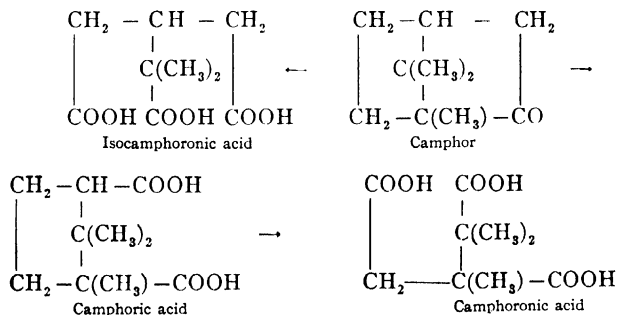camphoroxime and hydroxy-camphene (Forster).

3. *π-Derivatives*, in which a hydrogen atom is displaced from one of the central methyl groups. Substitution in this position can only be effected by sulphonation (Kipping and Pope).

Oxidation of Camphor.

The action of oxidising agents on camphor has been the subject of much research, and the products have great theoretical interest. By prolonged treatment with nitric acid of 1.37 sp. gr., camphor is chiefly converted into *camphoric acid*, $C_{10}H_{16}O_4$ (Kosegarten, 1785) which on further boiling is converted into *camphoronic acid*, $C_9H_{14}O_6$; iso-*camphoronic acid*, $C_9H_{14}O_6$, is also formed in small quantities as a by-product of the oxidation of camphor by nitric acid. The oxidation to camphoric acid is a simple change which does not involve the degradation of the molecule, and may be represented by the scheme

$$C_8H_{14}\underset{CO}{\overset{CH_2}{<}}| \longrightarrow C_8H_{14}\underset{CO.OH}{\overset{CO.OH}{<}}$$
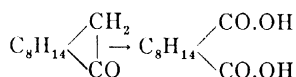
The reverse change from camphoric acid back to camphor has been effected by Haller (*Compt. rend.*, 1896, **122,** 446) and forms the the last stage in the synthesis of camphor from its elements by Kommpa's method. The oxidation to camphoronic and isocamphoronic acids is more complex, but both acids have been synthesised; the course of the oxidation is therefore quite clear, and it will be unnecessary to refer to the latter stages in the breaking down of the molecule whereby the constitution of these acids was first established.

$$\begin{array}{ccc} CH_2 - CH - CH_2 & \\ | \quad | \quad | & \\ \quad C(CH_3)_2 & \longleftarrow \\ | \quad | \quad | & \\ COOH\ COOH\ COOH & \end{array}$$
Isocamphoronic acid

$$\begin{array}{ccc} CH_2 - CH - CH_2 & \\ | \quad | \quad | & \\ \quad C(CH_3)_2 & \longrightarrow \\ | \quad | \quad | & \\ CH_2 - C(CH_3) - CO & \end{array}$$
Camphor

$$\begin{array}{c} CH_2 - CH - COOH \\ | \quad | \\ \quad C(CH_3)_2 \qquad \longrightarrow \\ | \quad | \\ CH_2 - C(CH_3) - COOH \end{array}$$
Camphoric acid

$$\begin{array}{c} COOH \quad COOH \\ | \qquad | \\ \quad C(CH_3)_2 \\ | \qquad | \\ CH_2 - C(CH_3) - COOH \end{array}$$
Camphoronic acid

It is noteworthy that in accordance with the above formulæ isocamphor-
onic acid, unlike camphoronic acid, can only be produced by direct
oxidation of camphor, and is not formed in the further oxidation of
camphoric acid.   Camphoric and camphoronic acids are also formed

on oxidising α-bromocamphor, $C_8H_{14}\diagdown\begin{smallmatrix}\diagup CHBr \\ | \\ \diagdown CO\end{smallmatrix}$, with nitric acid;

under similar conditions β-bromocamphor, $C_8H_{10}Br\diagdown\begin{smallmatrix}\diagup CH_2 \\ | \\ \diagdown CO\end{smallmatrix}$, gives

β-bromocamphoric acid, $C_8H_{13}Br\diagdown\begin{smallmatrix}\diagup COOH \\ \diagdown COOH\end{smallmatrix}$, while in presence

of silver nitrate *iso*-camphoronic acid is the main product; these
reactions are likewise in accord with the above formulæ, and are seen
to represent the normal course of oxidation in substances so constituted.
Camphoric acid appears again as the chief product of the oxidation of
camphor by potassium permanganate in the presence of caustic alkali;
neutral permanganate has but little action on camphor. Dilute
chromic acid mixture acts with difficulty on camphor, but by prolonged
treatment camphoronic and *iso*-camphoronic acids are produced.

   Camphoric acid, $C_8H_{14}(CO.OH)_2$, separates from alcohol in
monoclinic crystals which melt at 186°, and at a somewhat higher
temperature lose water and are converted into the anhydride.   Cam-
phoric acid dissolves in 160 parts of cold water or in 10 parts at the b. p.,
and is readily soluble in alcohol, ether, and fixed oils. From acetone
it crystallises with half a molecular proportion of acetone of crys-
tallisation (Pope).   It is employed in medicine for the treatment
of urinary calculi and vesical catarrh.   A 1% solution has been
recommended in acute and chronic affections of the respiratory pass-
ages.   Camphoric acid as ordinarily prepared is dextrorotatory
($[a]_D = +46°$), but a lævorotatory modification can be obtained
by the oxidation of lævo-camphor. The two varieties combine to
form an inactive racemic camphoric acid which melts at 204°, and is
less soluble than its isomerides. Inactive camphoric acid may also
be obtained by oxidising inactive camphor at 100° by nitric acid.

   Camphoric anhydride, $C_8H_{14}(CO)_2O$, prepared by heating the acid
alone or with acetic anhydride, crystallises from alcohol in magnificent
needle-shaped crystals, m. p. 217°; the preparation of the anhydride

affords an excellent method of characterising the acid. The *alkali* salts are freely soluble in water; the *calcium* salt, $CaC_{10}H_{14}O_4$ is moderately soluble; the salts of the heavy metals are insoluble in water. The *esters* prepared by condensing the anhydride with alcohols are oily liquids. The acid *phenyl ethers*, prepared by the action of their sodium derivatives on camphoric anhydride (Schryver, Trans., 1899, **75**, 663) are of interest as possible therapeutic agents:

Phenyl hydrogen camphorate, $C_6H_5O.CO.C_8H_{14}.CO.OH$, m. p.   100°
Thymyl hydrogen camphorate .... m. p.   89°
Guiacyl hydrogen camphorate .... m. p.   112°
Diguiacyl-camphorate .... m. p.   124°
Eugenyl hydrogen camphorate .... m. p.   115.5°
Naphthyl hydrogen camphorate .... m. p.   121–122°

Derivatives of Camphor; Ketonic Reactions.

Camphor does not form a compound with sodium hydrogen sulphite, this behaviour being, as a rule, limited to aldehydes and methyl-ketones, though some cyclic ketones show the same reaction. The *phenyl-hydrazone*, $C_{10}H_{16}:N.NHC_6H_5$, is an oil, and is therefore useless for separating or identifying the ketone. The *oxime*, $C_{10}H_{16}:NOH$, is, however, a crystalline compound, and may be used for the detection of camphor. It is formed when a solution of camphor in alcohol is treated with a concentrated aqueous solution of hydroxylamine hydrochloride, sodium carbonate added till the liquid is alkaline to litmus, and the solution diluted with alcohol and allowed to stand for 8 days. The liquid is then largely diluted with water, when the camphoroxime is precipitated; or the alcohol may be removed by evaporation and the residue extracted with ether. On evaporation of its ethereal solution camphoroxime crystallises in white needles, but from alcohol it separates in transparent prisms, which have an odour like camphor and gyrate on water. Camphoroxime melts at 118°, and boils with slight decomposition at 249°. It is nearly insoluble in water, but dissolves in alcohol, ether, solutions of alkali hydroxides, and acids.

The *semicarbazone*, $C_{10}H_{16}:N.NH.CO.NH_2$, is also a crystalline compound, m. p. 236–238°.,

Like the open-chain ketones described at the beginning of the section camphor possesses the property of forming an *enolic benzoyl-derivative*,

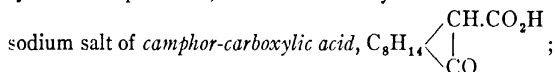$$C_8H_{14}\underset{C.O.CO.C_6H_5,}{\overset{CH}{<\ \|}}$$
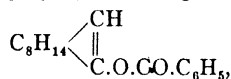
when boiled with benzoyl chloride (Lees, *Trans.*, 1903, **83**, 152); this is an oil boiling at 215 to 220° under 50 mm. pressure, and is slightly lævorotatory, giving α_D $-1°$ 5′ in a 25 mm. tube; when boiled with alcoholic potassium hydroxide it is converted into camphor and potassium benzoate, with hydroxylamine it gives camphoroxime and benzoic acid, with bromine it gives α-bromocamphor and benzoyl bromide.
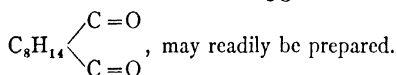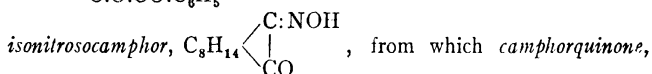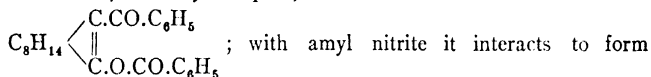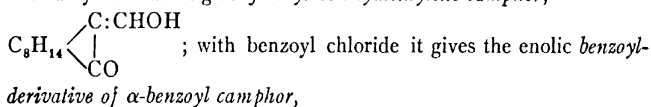
Sodium-camphor, prepared by the action of sodium or, better, of sodamide, on camphor dissolved in ether or benzene, is probably the enolic compound $C_8H_{14}\diagdown \begin{matrix} CH \\ \| \\ C.ONa \end{matrix}$.
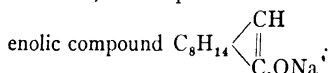
It is immediately decomposed by water, but is of importance in many synthetical operations; when acted on by carbon dioxide it gives the sodium salt of *camphor-carboxylic acid*, $C_8H_{14}\diagdown \begin{matrix} CH.CO_2H \\ | \\ CO \end{matrix}$;

with amyl formate it gives *formyl* or *oxymethylene camphor*, $C_8H_{14}\diagdown \begin{matrix} C:CHOH \\ | \\ CO \end{matrix}$; with benzoyl chloride it gives the enolic *benzoyl-derivative of α-benzoyl camphor*,

$C_8H_{14}\diagdown \begin{matrix} C.CO.C_6H_5 \\ \| \\ C.O.CO.C_6H_5 \end{matrix}$; with amyl nitrite it interacts to form

isonitrosocamphor, $C_8H_{14}\diagdown \begin{matrix} C:NOH \\ | \\ CO \end{matrix}$, from which *camphorquinone,*

$C_8H_{14}\diagdown \begin{matrix} C=O \\ C=O \end{matrix}$, may readily be prepared.

Like other ketones, camphor may be reduced to a secondary alcohol, the product being in this case a mixture of the 2 stereo-isomeric borneols represented by the formula

$$C_8H_{14}\diagdown \begin{matrix} CH_2 \\ | \\ CH.OH. \end{matrix}$$
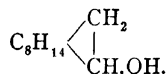
The reduction does not take place readily, but may be effected by the action of sodium and alcohol.

α-Derivatives of Camphor.

$$\alpha\text{-}Bromocamphor, \quad C_8H_{14}\!\!\left\langle\begin{array}{l} CHBr \\ | \\ CO \end{array}\right.,$$
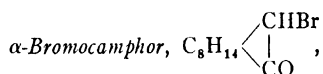
is prepared by heating camphor on a water-bath, and slowly running in slightly more than 1 molecular proportion of bromine, the hydrogen bromide which is liberated being condensed with water in a coke-tower. After driving off as much as possible of the hydrogen bromide, the hot and oily material is shaken with a little aqueous potassium hydroxide, poured into a large quantity of water, and recrystallised from alcohol. It separates in long needles, and when pure has m. p. 76° and b. p. 274°. It may be distilled without much decomposition, but the distillation is best carried out under reduced pressure or by means of a current of steam. Bromocamphor is nearly insoluble in water, sparingly soluble in glycerin, moderately (1:8) in olive oil and 90% alcohol (1:12), and readily soluble in ether, chloroform, and benzene.

It is strongly dextrorotatory, giving $[\alpha]_D + 139°$ in saturated alcoholic solution.

When boiled with a solution of silver nitrate, it is decomposed, a precipitate of silver bromide being formed. Bromocamphor is soluble without decomposition in cold concentrated sulphuric acid, and is precipitated unaltered when the solution is poured into excess of water. When treated in alcoholic solution with potassium hydroxide or sodium amalgam, bromocamphor is reduced to camphor. When treated with sodium in toluene solution, it yields sodium-camphor. Bromo-camphor is employed in medicine as a sedative and hypnotic, and has been found specially useful in cases of hysteria, dipsomania, and delirium tremens. It is official in the United States Pharmacopœia and in most others except the British.

$$\alpha\alpha'\text{-}Dibromocamphor, \quad C_8H_{14}\!\!\left\langle\begin{array}{l} CBr_2 \\ | \\ CO \end{array}\right.,$$
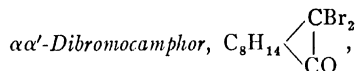
prepared by acting on camphor with 2 molecular proportions of bromine, crystallises from alcohol, m. p. 61,° and gives $[\alpha]_D + 40°$ in nearly all solvents; it is very readily reduced to α-bromocamphor by alcoholic sodium or potassium hydroxide.

$$\alpha\alpha'\text{-}Bromonitrocamphor, \quad C_8H_{14}\!\!\left\langle\begin{array}{l} CBr.NO_2 \\ | \\ CO \end{array}\right.,$$

prepared by the action of nitric acid on α-bromocamphor (about half the bromocamphor is oxidised to camphoric acid, and half nitrated), has m. p. 107°, and gives $[\alpha]_D - 22.0°$ when dissolved in chloroform, $[\alpha]_D - 54°$ in benzene.

$$\alpha'\text{-}Nitrocamphor, \quad C_8H_{14} \underset{\diagdown CO}{\overset{\diagup CH.NO_2}{\Big\langle}} \; , \quad prepared \; by \; reducing$$

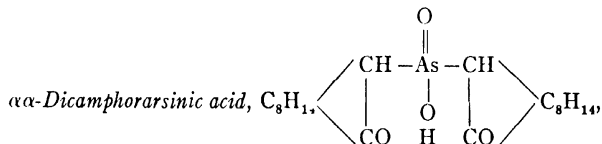$\alpha\alpha'$-bromonitrocamphor in alcoholic solution with sodium ethoxide (camphor cannot be nitrated directly), m. p. 102°. Although itself lævorotatory, it forms a series of strongly dextrorotatory *salts*, and a dextrorotatory *anhydride*, m. p. 196°, derived from a hydroxylic isomeride,

$$C_8H_{14} \underset{\diagdown CO}{\overset{\diagup C:NO_2H}{\Big\langle}} \qquad . \; A \; partial \; conversion \; of \; the \; normal \; compound \; into$$

the acidic isomeride takes place in solution and is accompanied by a change of rotatory power from left toward right, *e. g.*, in benzene from $-124°$ to $-104°$.

$$\alpha\text{-}Chlorocamphor, \quad C_8H_{14} \underset{\diagdown CO}{\overset{\diagup CHCl}{\Big\langle}} \; ,$$

prepared by the action of chlorine on camphor dissolved in alcohol, crystallises from alcohol in long glistening needles, m. p. 93°, and gives $[\alpha]_D + 96°$ in alcohol.

$$\alpha\alpha\text{-}Dicamphorarsinic \; acid, \; C_8H_{14} \underset{\diagdown CO \quad H \quad CO \diagup}{\overset{\diagup CH - As - CH \diagdown}{\Big\langle}}\;{\overset{\overset{\textstyle O}{\|}}{}}\;{\overset{\textstyle |}{O}}\; C_8H_{14},$$

prepared by the action of arsenious chloride on sodium camphor, is almost insoluble in water, but separates from alcohol in lustrous prisms, m. p. with decomposition 266°; $[\alpha]_D + 186.6°$ in chloroform. The *alkali* salts dissolve readily in water; the *silver* and *cadmium* salts are sparingly soluble crystalline precipitates (Morgan and Mickelthwaite, *Trans.*, 1908, **93,** 2144–2148).

β-Derivatives of Camphor.

Camphor β-sulphonic acid, $C_{10}H_{15}O.SO_2OH$, separates in a crystalline form when a mixture of camphor (1 mol.) acetic anhydride (2 mols.), and sulphuric acid (1 mol.) is allowed to stand for 2 or 3 days

(Reychler); it is readily soluble in water, from which it separates with $1H_2O$, crystallises well from acetic acid or ethyl acetate, m. p. 193°, and gives $[\alpha]_D + 21°$ in water. The *amide*, $C_{10}H_{15}.SO_2.NH_2$, has m. p. 132°, and the *anhydramide*, $C_{10}H_{15}SO_2N$, formed by removal of a molecule of water from the amide, melts at 223°. The *sulphochloride*, $C_{10}H_{15}SO_2Cl$, has m. p. 68°; the *sulphobromide*, $C_{10}H_{15}O.SO_2Br$, melts at 93°, and when heated in boiling xylene loses sulphur dioxide and gives β-bromocamphor.

β-Bromocamphor, m. p. 78°, gives $[\alpha]_D + 19°$ only; it can be distinguished from the α-isomeride most readily by determining the m. p. of a mixture with the α-compound; this mixture melts at a much lower temperature than either of the isomerides separately.

$$\alpha\beta\text{-}Dibromocamphor,\ C_8H_{13}Br \left\langle \begin{array}{l} CH.Br \\ | \\ CO \end{array} \right. ,\ \text{prepared by brominating}$$

camphor in a sealed tube (when the HBr converts the $\alpha\alpha'$ into the $\alpha\beta$ compound), by brominating the preceding compound, or by decomposing α-bromocamphor β-sulphobromide, has m. p. 113°.

β-Chlorocamphor, prepared by Forster's method, melts at 132.5°.

α-Chloro β-bromocamphor, prepared in much the same way as the dibromocompound, has m. p. 98°.

Camphor β-thiol, prepared by reducing the β-sulphochloride with tin and hydrochloric acid, melts at 66°, gives $[\alpha]_D + 6°$ in acetone.

π-Derivatives of Camphor.

Camphor π-sulphonic acid, $C_{10}H_{15}O.SO_2.OH$, prepared by the action of chlorosulphonic acid on camphor, is most readily separated in the form of the *ammonium* salt. The *amide*, $C_{10}H_{15}O.SO_2.NH_2$, has m. p. 135–137.5°, and forms an *acetyl*-derivative, m. p. 199°. The *sulphochloride*, $C_{10}H_{15}O.SO_2Cl$, melts at 137.5°, losing a molecule of sulphur dioxide and giving *π-chlorocamphor*, $C_{10}H_{15}ClO$, m. p. 139°. The *sulphobromide*, $C_{10}H_{15}O.SO_2Br$, melts in a similar manner at 145° with formation of SO_2 and *π-bromocamphor*, $C_{10}H_{15}BrO$, m. p. 93°.

α-Chlorocamphor gives a *sulphonamide* m. p. 150°, a *sulphochloride* m. p. 124°, and a *sulphobromide* m. p. 145°, the products arising from the fusion of the latter compounds being SO_2 and *απ-dichlorocamphor* m. p. 118°, or *απ-chlorobromocamphor*, m. p. 138°.

α-*Bromocamphor* π-*sulphonic acid* has been extensively used for resolving racemic bases into their optically active constituents. The *sulphonamide*, has m. p. 145°; the *sulphochloride*, m. p. 136–137°, and the *sulphobromide*, melts at 145°, giving SO_2 and απ-*bromochlorocamphor*, m. p. 133°, or απ-*dibromocamphor*, m. p. 152–153°.

Cyclic Ketones.   Homologues of Camphor.

α-*Methyl-camphor*, $C_8H_{14}\begin{cases} CH.CH_3 \\ | \\ CO \end{cases}$, prepared by hydrolysing

methyl α-methylcamphorcarboxylate,

$C_8H_{14}\begin{cases} C(CH_3).CO.OCH_3 \\ | \\ CO \end{cases}$, has m. p. 38°, b. p. 215–218°, and gives

$[\alpha]_D + 30°$ in alcohol.

The *oxime* melts at 55° and gives $[\alpha]_D + 30°$ in alcohol.   It can be sulphonated by Reychler's method, the β-*sulphonamide*, melting at 150°, and the *anhydramide* at 167.5° (Glover, *Trans.*, 1908, **93**, 1297).

Matico-camphor, $C_{12}H_{20}O$,[1] occurs in the essential oil obtained from the leaves of the narrow-leaved pepper (*Piper angustifolium*) of South America, which are employed locally for small wounds, such as leech-bites.   After purification from admixed resins by repeated crystallisation, the camphor forms hexagonal crystals, is colourless and odourless, m. p. 94°, has $[\alpha]_D$ —28.73°, and gyrates like common camphor when thrown onto water.   Matico-camphor is not attacked by aqueous alkalies, but is readily soluble in alcohol, ether, chloroform, benzene, and petroleum spirit.

According to K. Kügler (*Ber.*, 1883, **16**, 2841), in contact with hydrochloric acid matico-camphor assumes an intense violet colour, which changes to blue and then to green, and on extraction with ether a compound is obtained which forms brown crystals and exhibits a green fluorescence.   With strong sulphuric acid, matico-camphor becomes yellow, then red, and finally violet.   With a mixture of sulphuric and nitric acids it assumes a yellow colour, changing to violet and finally to blue.

Cyclic Ketones, $C_{10}H_{16}O$.   Fenchone, Pulegone, and Thujone.

Isomeric with camphor is a series of three liquid ketones—fenchone, pulegone, and thujone.

[1] Thomas (*Apoth. Zeit.*, **19**, 771–773) states that matico-camphor is a sesquiterpene alcohol, $C_{15}H_{26}O$, since on boiling with a 50% solution of sulphuric acid it forms a sesquiterpene with elimination of water.

Fenchone, $C_{10}H_{16}O$, discovered by Wallach in 1890, is an important constituent of fennel oil (from *Faniculum vulgare*), whilst a lævorotatory form occurs with the isomeric ketone thujone in Thuja oil. It has b. p. 192° to 194°, m. p. 5°, and sp. gr. 0.9465 at 19°. The values obtained for the rotatory power of the isomerides were +72° and −67°. It differs from camphor in being very resistant both to nitric acid and to bromine, does not react with phenylhydrazine or sodium hydrogen sulphite, does not form an oxymethylene derivative and cannot be sulphonated by Reychler's method. Phosphoric oxide converts it into *m*-cymene, where camphor gives *p*-cymene, and the formula

$$CH_2-CH - CH-CH_3$$
$$C(CH_3)_2$$
$$CH_2-CH - CO$$
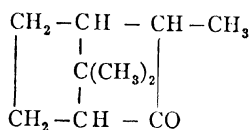
has therefore been proposed by Wallach (*Annalen*, 1898, **300,** 319). As, however, its behaviour is entirely different from that of α-methyl-camphor, this formula can scarcely be upheld, and Glover (*Trans.*, 1908, **93,** 1286) has suggested the formula
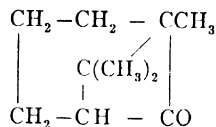
$$CH_2-CH_2 - CCH_3$$
$$C(CH_3)_2$$
$$CH_2-CH - CO$$

Fenchone shows the normal properties of a ketone: the *oxime* has m. p. 165°; the *semicarbazone*, m. p. 186–387°, and the secondary alcohol *fenchyl alcohol*, $C_{10}H_{17}OH$, prepared by the action of sodium and alcohol, m. p. 45°, b. p. 201°, and a rotatory power $[\alpha]_D \pm 10.6°$, the alcohol being opposite in sign to the ketone.

Pulegone, $C_{10}H_{16}O$.

Pulegone is the chief constituent of oil of pennyroyal (from *Mentha pulegium*). Unlike the preceding compound, it forms a *bisulphite-compound*, which may be utilised in the isolation of the ketone. It is a colourless oil, b. p. 221°, sp. gr. 0.936, has an odour like that of peppermint, and turns yellow on exposure to air. Its constitution has been established by synthesis (Tiemann and Schmidt, *Ber.*, 1896, **29,** 913).

$$CH_3.CH \underset{\displaystyle CH_2-CH_2}{\overset{\displaystyle CH_2-CO}{\diagdown}} C=C \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\diagdown}}$$
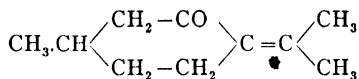
In accordance with this formula, it is converted by reduction into menthone and menthol, and by oxidation into β-methyladipic acid,

$$CH_3.CH \underset{\displaystyle CH_2-CH_2}{\overset{\displaystyle CH_2-COOH}{\diagdown}} CO.OH \quad \text{and} \quad CO \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\diagdown}}$$
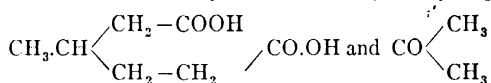
The *oxime* melts at 120° to 121° and the *semicarbazone* at 172°.

For the detection of pulegone, equal volumes of the ketone and petroleum-ether are mixed with a little amyl-nitrite, the mixture cooled thoroughly, and a drop of hydrochloric acid added. If pulegone be present, white nitrosopulegone separates and the liquid becomes blue in colour. 1% of pulegone may thus be detected.

Thujone or Tanacetone, $C_{10}H_{16}O$.

Thujone is a ketone present in the oils of thuja, tansy, and wormwood, and is apparently identical with the *salvone* or *salviol* of oil of sage. It may be prepared conveniently by treating 200 grm. of wormwood oil with 200 c.c. of a saturated solution of sodium hydrogen sulphite, 75 c.c. of water, and 300 of alcohol. The mixture is shaken at intervals for a fortnight, when the crystals of the addition compound which separate are washed with ether-alcohol, and the thujone set free by sodium hydroxide solution.

It is an oil, b. p. 200° and sp. gr. 0.917.

Thujone forms a tribromo-derivative, $C_{10}H_{13}Br_3O$, m. p. 121°, an oxime, m. p. 55°, and a carbazone, m. p. 171°. By treatment in alcoholic solution with sodium, it is almost entirely converted into *thujyl alcohol*, $C_{10}H_{17}.OH$, an isomer of linalol occurring in oil of tansy.

Prolonged heating with strong sulphuric acid converts thujone into *isothujone;* and when heated alone to 280°, thujone is converted into another isomer called *carvotanacetone.*

Ketones, $C_{10}H_{14}O$.

Carvone.

$$CH_3.C \underset{\displaystyle CO-CH_2}{\overset{\displaystyle CH-CH_2}{\diagxup}} CH-C \underset{\displaystyle CH_2}{\overset{\displaystyle CH_3}{\diagdown}}$$
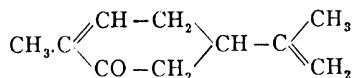
A doubly-unsaturated cyclic ketone, formerly known as carvol, occurs both in the dextrorotatory and in the lævorotatory form.

d-Carvone occurs to the extent of 50% in oil of caraway, together with nearly as much limonene. It is also present to the extent of 30% in the oils of dill and fennel, while *lævo-carvone* occurs in the oil of *Mentha crispa*.

Pure dextro-carvone may be prepared by treating the fraction of caraway oil distilling above 190° with an equal volume of alcoholic ammonium sulphide, when a substance of the composition $C_{10}H_{14}$-(OH).(SH) separates in long needles, which on treatment with alcoholic potassium hydroxide are decomposed with separation of carvone.

Carvone is official in the German Pharmacopœia (carvol), in which it is described as a pale yellowish or colourless liquid, having a strong odour of caraway. The sp. gr. is given as o.960 and the b. p. as 224°. 1 c.c. of carvone diluted with an equal measure of alcohol is stated to remain unchanged or to assume only a slight or violet colour on addition of a drop of a very dilute solution of ferric chloride. Pure carvone has the practical advantage of being much more readily soluble in dilute alcohol than is the case with oil of caraway, while it possesses all the valuable properties of the natural oil.

Carvone shows all the characteristic reactions of a ketone. The *oxime*, $C_{10}H_{14}$:NOH, m. p. 72°, is identical with nitrosolimonene, indicating a close relationship between the two parent substances; it forms a *benzoyl* derivative, m. p. 95°. The *semicarbazone* melts at 162 to 163°.

When boiled with excess of sodium hydrogen sulphite, the ketone is converted into a substance which, according to Labbé, has the formula $C_{10}H_{14}O(SO_3NaH)_2$.

On treating it with metaphosphoric acid, great heat is evolved and actual explosion is apt to occur. With crude caraway oil the action is less intense. In either case, the ketonic substance carvone is converted into the isomeric substance *carvacrol*, a phenol of the formula

CH_3—⟨ ⟩—$CH(CH_3)_2$ (with HO on the ring) derived from the hydrocarbon *p*-cymene

and differing from thymol only in the orientation of the hydroxyl group.

Carvacrol occurs in several essential oils, especially those of the thyme family. It is the principal constituent (50 to 80%) of Spanish oil of hops, of Cretan oil of marjoram (from *Origanum hirsutum* and

creticum), and also occurs abundantly in the oils of caraway and pepper-wort (*Satureja hortensis*). In smaller quantity, carvacrol exists, together with thymol and cymene, in the oil from *Thymus serpyllum*.

The carvacrol occurring naturally in essential oils is probably a product of the molecular transformation of previously existing carvone, the—CH.CO—group being rearranged to form the—C:C(OH)— group. The same change can be effected by heating carvone with alcoholic potassium hydroxide.

Carvacrol is a thick, oily liquid of peculiar aromatic odour. On cooling in a freezing mixture, it forms crystals, m. p. about 1°.

The alcoholic solution of carvacrol is not coloured green by ferric chloride until after addition of water (distinction from carvone). With phosphoric anhydride, carvacrol yields propylene and *p*-cresol.

Estimation of Carvone.

The estimation of this important constituent of certain essential oils (*e. g.*, the oils of caraway, cumin, dill, spearmint, etc.) cannot be made with any degree of accuracy. Several methods have been proposed, as, for example, those based on a determination of the iodine absorption of the oil, and on the results obtained by fractional distillation. Neither of these processes, however, gives a reliable indication of the carvone content. The sp. gr. and the optical rotation of the carvone-containing oils are, of course, valuable data, but give only a rough approximation to the percentage of carvone.[1]

A promising method for the estimation of carvone, based on the formation of a crystalline carvoxime, has been proposed and studied by E. Kremers (*J. Soc. Chem. Ind.*, 1901, **20**, 16) and his collaborators (*Pharm. Rev.*, 1896, 76; *Pharm. Arch.*, 1899, **2**, 81–91; 1900, **3**, 9–18).

[1] Assuming that caraway oil contains only limonene and carvone, and that *a* represents the sp. gr. of the sample, the percentage of carvone (*x*) may be deduced from the following formula:

$$x = \frac{(a - 0.850)\,100}{0.112}$$

0.850 is the sp. gr. of limonene, and 0.112 the difference between this and the sp. gr. of carvone (0.962).

A process in which the crystalline hydrogen sulphide addition product is isolated and the carvone regenerated and weighed, is rendered useless as a quantitative method by the fact that the carvone hydrosulphide remains partly in solution, and also other constituents in the oils are apparently acted on by hydrogen sulphide.

Another method which has been largely employed for the estimation of carvone is that in which the crystalline carvone-phenyl-hydrazone, resulting from the reaction of the carvone with phenyl-hydrazine at 100°, is isolated and weighed after purification. The compound, however, is unstable and cannot be dried without decomposition, and the method thus gives only approximate results.

See also Alden and Ehlert, *Chem. Centr.*, 1897, ii, 146. A known
weight of the oil under examination, containing about 5 grm. of carvone,
is dissolved in 25 c.c. of alcohol, and 5 grm. of hydroxylamine hydro-
chloride and 6.5 grm. of sodium hydrogen carbonate are added.[1] The
mixture is boiled for 15 to 20 minutes on the water-bath under a
reflux condenser; 25 c.c. of water are next introduced, and the alcohol
is distilled off, a large quantity of limonene simultaneously passing over.
Steam is then passed slowly through the flask and the distillation con-
tinued, collecting the last portions of the distillate in separate test-
tubes till traces of carvoxime crystals appear on the surface of the
liquid.[2] The distillation is stopped, the condenser rinsed with a
little hot water, which, together with the last distillates, is returned to
the flask. The whole is cooled, and when the oxime has solidified it is
collected on a filter (removing what adheres to the flask by means
of a loop of stiff wire), washed, and dried by suction. The air-dried
product is finally heated for 1 hour on the water-bath and weighed.
To the weight thus obtained 0.100 grm. is added to compensate for
the loss by volatilisation and the carvoxime so corrected is calculated
into carvone by the factor 0.9088.[3] The method gives results which
are fairly uniform, but are usually about 2% too low. It is necessary
that the directions should be strictly followed to obtain satisfactory
results. Kremers considers the method by no means perfect, but of
much value, and it has the advantage of yielding a definite crystalline
compound.

When an oil is badly resinified, the carvoxime may refuse to crys-
tallise, and in such case the oil should be distilled with steam, and
the process carried out on the distillate. A small quantity of resin
will increase the weight of oxime recovered, and so tend to make the
results too high. The m. p. of the carvoxime, which should lie
between 71° and 73°, is lowered by the presence of resin, but no idea
of the amount of impurity can be obtained in this way, as the point
at which melting begins in the impure oxime is not sharp.

[1] It is desirable not to use more sodium hydrogen carbonate than is necessary to liberate
the whole of the hydroxylamine. Kremers' experiments, indeed, show that the amount of
sodium bicarbonate may be advantageously reduced to 5.5 grm. instead of employing 6.5
grm. as recommended in the text. A large excess of hydroxylamine hydrochloride should
be avoided. If more than 50% of carvone is supposed to be present, the amount of hy-
droxylamine is correspondingly increased.
[2] If the distillation of the carvoxime and alcohol mixture is not carried out carefully in
the manner described, loss may be entailed by carrying the distillation too far. Schimmel
& Co. failed to obtain satisfactory results by this method (Semi-Annual Report, October,
1896, p. 49), probably for this reason.
[3] The volatility of carvoxime in presence of water-vapour is somewhat irregular, and the
drying of the compound should always be conducted under similar conditions.

J. Walther (*J. Pharm. Chim.*, 1901, **13**, p. 32) has proposed to estimate carvone by titrating the excess of hydroxylamine hydrochloride remaining after the removal of the carvoxime.

For the separation of carvone from limonene, H. Labbé (*Bull. Soc. Chim.*, 1900, **23**, 280) boils together 5 grm. of the oil and 15 of sodium hydrogen sulphite, with water and some sodium bicarbonate, for 1.5 hours in a small flask fitted with a reflux condenser. The product is shaken out with ether, the separated ethereal layer dried by anhydrous sodium sulphate, and the residual limonene, etc., weighed. The carvone is estimated by difference.

Eucarvone and isocarvone are two ketones isomeric with carvone; the former gives an *oxime*, m. p. 106°, and a *semicarbazone*, m. p. 184°; the latter gives an *oxime*, m. p. 98°; neither compound has been detected as a natural product.

VOLATILE OR ESSENTIAL OILS.[1]

By ERNEST J. PARRY, B. Sc., F. I. C.

The great majority of the products known as *essential oils* are proxi-
mate principles occurring in nature ready-formed, or as glucosides
which by the action of water or enzymes readily undergo decomposi-
tion into essential oils and one or more other substances. The char-
acteristic odours of plants are due, in nearly every case, to the presence
of essential oils.

Broadly speaking, the essential oils differ from the fixed or fatty
oils by being volatile without leaving any fixed residue. Hence they
do not produce a permanent, translucent, oily mark on paper. In
most cases also the essential oils possess strong and characteristic
odours. For general purposes this distinction is sufficient. But
it must be remembered that many essential oils are mixtures of a
preponderating amount of constituents which are volatile without
decomposition, together with a certain amount of fixed non-volatile
matter which has either been mechanically carried over in the distilla-
tion (such as is the stearoptene of otto of rose), or which results
from the oil having been prepared by expression (as in the case of ber-
gamot oil). Further, although most essential oils are volatile without
decomposition, many cannot be distilled under ordinary pressure with-
out some decomposition occurring, and must therefore be distilled
under reduced pressure or in a current of steam.

Extraction of Essential Oils.

The volatile oils of plants are obtained:

a. By expression, as the oils of lemon and bergamot.

b. By *distillation with water*, or by passing a current of *steam* through
the matter to be extracted. This is the most common and generally
applicable method.

[1] French: *Huiles Essentielles, Essences.* German: *Flüchtige Oele.*

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c. By *fermentation and distillation;* as, for instance, with the essential oils of mustard and bitter almonds, the seeds containing no ready-formed essential oil, the latter being produced when the crushed seeds are left in contact with water, owing to the influence of peculiar nitrogenised ferments, the oil formed being then separated by distillation with water.

d. By *solution in a fixed oil* devoid of odour, such as olive oil or lard (the "enfleurage" process). The perfumes of the more delicate plants are extracted in this manner, such as the violet, cassia, and tuberose.

e. By *extraction with a volatile solvent* and recovery of the volatile solvent by distillation. This process is only used in the case of delicate oils which may not be exposed to high temperatures.

Many of the oxygenated and sulphuretted constituents of essential oils have been prepared synthetically.

Composition of Essential Oils.

Essential oils are usually of very complex composition, and different specimens from the same botanical source often exhibit considerable variations in the proportions of their constituents. These variations are due to many external conditions, such as climate, soil, method of cultivation, etc. A leading example of such a variation may be found in plants of the Labiate family, such plants as peppermint or lavender yielding entirely different oils according to the district in which they are cultivated. An English lavender oil will be found to contain less than 10% of esters, whereas if the same plants be transplanted to France the ester value of the oil will gradually increase up to 35% or more. The age of the plant is also an important factor in the composition of an essential oil, as the same plant gathered when immature and when ripe may yield quite different essential oils.

The only satisfactory classification of essential oils is according to their botanical origin. The alternative method, adopted by many French chemists, is to classify them according to their chemical relationships. But this at once raises a serious difficulty. Many oils owe their chief characteristics to at least two different substances. For example, citronella oil contains a large amount of both geraniol and of citronellal. If we adopt a chemical classification, are we to place this oil with otto of rose, which contains a very large amount of geraniol, or with a lemon-grass oil, which consists chiefly of the aldehyde citral. Both

German and English chemists prefer a botanical classification, and this will be found to have considerable advantages over a chemical one. The greater part of the essential oils will be found to owe their principal characteristics to one or more of the following groups of compounds:

1. *Terpenes*, hydrocarbons of the formula $C_{10}H_{16}$: in many of these cases 90% of terpenes are present, but they are seldom the most useful portion of the oil, which frequently depends entirely for its value on the remaining constituents, *e. g.*, lemon oil, orange oil.

2. *Sesquiterpenes*, hydrocarbons of the formula $C_{15}H_{24}$: cedar-wood oil and patchouli oil are types of this class.

3. Open-chain *alcohols* and their corresponding *aldehydes:* such are the so-called Indian grass oils (citronella, lemon-grass and Indian geranium oils).

4. *Aromatic alcohols* of the *Camphor series* and their corresponding ketones, such as peppermint, thuja, and pennyroyal oils.

5. *Aromatic alcohols* of the *Benzene series* and their corresponding *aldehydes* and *ketones*, such as bitter-almond oil, caraway oil, and cinnamon oil.

6. *Sesquiterpene alcohols*, such as sandalwood oil.

7. *Phenols* and their derivatives, such as clove and aniseed oils.

8. *Esters* of any of the above-mentioned alcohols, such as lavender and bergamot oil, wintergreen oil.

9. *Sulphur compounds*, such as garlic oil.

There are a few oils which do not come under any of these heads, but they are not very numerous.

General Characters of Essential Oils.

The essential oils of plants are usually liquid at ordinary temperatures, but many of them deposit solid bodies called *stearoptenes* by sufficient cooling, *e. g.*, camphor, and the paraffin hydrocarbons of rose oil. The essential oils have marked, and in many cases characteristic, odours. They volatilise slowly at ordinary temperatures, though their b. p. are mostly somewhat high. Essential oils are usually colourless or yellow when freshly prepared, but a few have well-marked colours. Some oils rapidly darken on exposure to air and light. Oils which contain aromatic aldehydes often deposit crystals of the corresponding acids on exposure to air.

Those volatile oils which consist chiefly of terpenes are very prone to

change in contact with air and moisture, especially in presence of light. The chief products of such change are ill-defined resinous substances the chemistry of which is but little understood. There is no evidence of the conversion of the hydrocarbons into any of the normal odorous constituents of such oils. On the contrary, Charabot has adduced evidence that, in some cases, the terpenes result from the dehydration of preformed alcohols, during the development of the plant.[1]

Most of the essential oils are optically active. In a number of cases the rotatory power only varies between well-defined limits, so that this function is of great value in the examination of the oils.

All essential oils possess somewhat high refractive indices. Taken at 20°, this figure will be found to vary from about 1.4600 to 1.5100, with a few oils outside these limits. For example, oil of rue has a refractive index of about 1.4350, while oil of bitter almonds reaches ι 45560. The value of optical methods for essential oils cannot be overestimated, but their limitations must be recognised. If a given sample shows values which are outside the well-established limits, adulteration may be presumed, but oils may easily be skilfully adulterated so that they will show the same values as those for pure oils. Hence when the values are within prescribed limits, they must only be taken as confirmatory. It must be remembered, too, that the optical values found are the mean of those of numerous optically active constituents, and an optically inactive oil may consist of a number of dextrorotatory and lævorotatory substances so balanced as to produce an optically inactive mixture. The separation of an oil into fractions by distillation under reduced pressure is essential in many investigations. The optical characters of the various fractions will, in the hands of a skilled operator, indicate much that is not suggested by the observation of the optical characters of the oil itself.

The sp. gr. of the essential oils mostly range between 0.850 and 0.990; but some few have sp. gr. below 0.850, such as oil of hops (0.840), while others are considerably heavier than water, such as oil of wintergreen (1.187). The sp. gr. of some essential oils are liable to variations with the age of the samples and other conditions.

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[1] Charabot considers that the formation of the chief constituents takes place in 2 stages, the first of which determines the elaboration of alcohols, which by the elimination of water or by esterification are converted into terpenes and esters, respectively. The second stage he regards as coincident with the period during which the respiratory energy is brought to bear on the processes of assimilation, when the quantity of oxygen fixed is sufficient to convert the primary alcohols into aldehydes and the secondary into ketones.

The essential oils are all readily combustible. They are in most
cases insoluble, or nearly so, in water, but distinct traces of some of
them pass into solution, the water acquiring the characteristic taste
and odour of the oil.[1] In alcohol they are freely soluble, and are
reprecipitated from their solutions by dilution with water. The sepa-
ration, however, is rarely, if ever, complete. The essential oils are
miscible in all proportions with fixed oils, oil of turpentine, light
petroleum, and carbon disulphide, and may be separated from aqueous
liquids by agitation with these solvents.

On cooling natural essential oils, the solid principles forming the
stearoptenes often crystallise out.[2] On distilling an oil thus freed from
substances of high m. p. the more volatile hydrocarbons first pass over,
and on raising the temperature the remainder of the stearoptene may
also be obtained in some cases, the non-volatile residue consisting
either of non-volatile solid matter which has been carried over mechan-
ically in the original distillation, or of products of oxidation of the oil,
frequently of a resinous nature. The more volatile portion of the
distillate may be freed from oxygenated compounds by redistillation
over sodium, and the hydrocarbons, when present, thus obtained pure.

It is to the presence of oxygenated constituents that the characteristic
aroma, flavour, and medicinal value of most essential oils are chiefly,
if not entirely, due, the hydrocarbons having but little value in these
respects and acting chiefly as diluents. Hence so-called "terpeneless"
or "concentrated" essential oils are now prepared by careful fractional
distillation of the crude oils.   The terpenes have a lower b. p. than the
valuable alcohols, aldehydes, etc., and hence pass over first, while the
fractions of higher b. p. are more powerful in odour and flavour than
the entire oil, owing to the removal of the greater part of the compara-
tively valueless terpenes.[3]

Since the value of the oxygenated constituents of essential oils has
become more generally recognized, methods for estimating the pro-
portion present in the oils and of isolating some of them in an approxi-
mately pure state have come into use, and certain of them have received

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[1] Dragendorff states that 1 litre of water holds in solution the following quantities of
essential oils: Oil of cloves, 1.5 grm. oil of rosemary, 0.9; oil of lavender, 0.5; oil of pepper-
mint, 0.2; oil of savin. 0.5; oil of copaiba, 0.12; and oil of bitter-almonds, 2.2 grm.

[2] Schimmel & Co. (Report, Oct. 1898) employ a modification of Beckmann's freezing-point
apparatus for the determination of the solidifying-point of the oils of anise, fennel, etc.

[3] By careful fractionation, lemon oil can be separated into about 95% of terpenes and
5% of oxygenated compounds (chiefly citral and esters of geraniol). The distillation is
necessarily conducted under reduced pressure, since too high a temperature leads to de-
composition of some of the oxygenated constituents.

official recognition in the pharmacopœias of recent date. These
analytical methods are described at length in the sequel.

Analysis of Essential Oils.

The isolation or estimation of the various constituefits of essential
oils is often extremely difficult, and not unfrequently impossible.
Much advance, however, has been made in this direction of late years,
and though no generally applicable or systematic method of analysis
can be prescribed, in many cases it is now quite feasible to ascertain
by comparatively simple methods the presence and approximate pro-
portion of the constituent on which the value of an essential oil depends.
Thus, by agitating the oil with a 5% solution of alkali hydroxide, the
phenols in such oils as clove and thyme can be approximately estimated.
By boiling with alkali hydroxide in alcoholic solution, any *esters* will
undergo saponification. Boiled with sodium hydroxide and lead
acetate, the *sulphuretted oils* (*e. g.*, oils of garlic and mustard) give
black lead sulphide. Oils containing aromatic *aldehydes* precipitate
metallic silver from an ammoniacal solution of the nitrate. The
aldehyde may be approximately separated from the other constituents
by agitating the oil with a strong aqueous solution of sodium hydrogen
sulphite, when (1) a crystalline compound is formed from which the
remaining oil may be separated by agitation with ether; or (2) the
crystalline aldehyde-sulphite compound dissolves in the excess of
sulphite solution, and the lighter non-aldehydic portion of the oil may
be readily separated from the lower aqueous layer.

The foregoing classes of constituents having been separated as
completely as possible, the chemically indifferent compounds can then
be more advantageously dealt with.

Fractional distillation affords one of the simplest and best means
of effecting a rough proximate analysis of essential oils. The process
should be conducted systematically, and under conditions as little
variable as possible. The use of a Wurtz flask is generally sufficient
to separate the necessary fractions, but it is undesirable to prolong the
operation of distillation longer than is absolutely necessary, since
polymerisation or other change is liable to occur by long exposure to a
high temperature.

In the analysis of essential oils and allied substances, it is frequently
necessary to distil the liquid under examination at a reduced pressure,

or even *in vacuo*, or by means of a current of steam. For example, in the estimation of the citral in lemon oil by Parry's process (page 271), the oil must first be concentrated by distilling off the greater part of the terpenes at a pressure of about 12 mm. In the apparatus
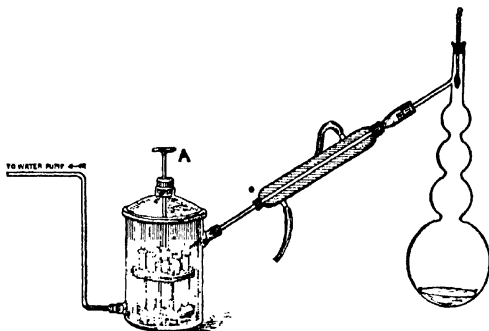

FIG. 1.
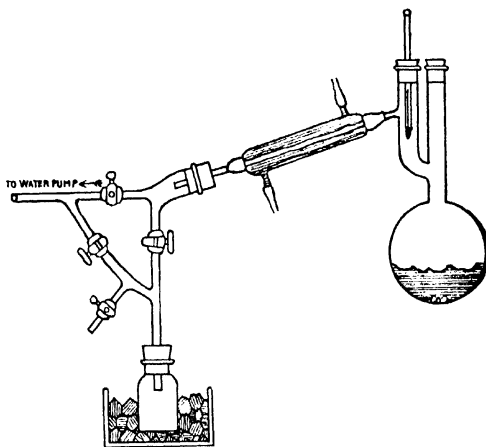
FIG. 2. Apparatus for distillation under reduced pressure.

shown in Fig. 1 the distillate drops into a series of test-tubes which can be revolved at will by turning the handle A of the Brühl's jar, without breaking the vacuum.

An alternative form of apparatus (Fig. 2) is that recommended

by Fischer and Harries (*Ber.*, 1902, **35,** 2158). The glass-tube triangle, fitted with four stop-cocks, enables the receiver to be changed by letting in air to equalise the pressure, without destroying the vacuum in the apparatus. This arrangement is also more convenient than a Brühl's jar, which takes some time to exhaust.

Detection of Sulphur Compounds in Essential Oils.

Sulphuretted bodies, such as form the major parts of the oils of garlic and mustard, may be detected by boiling the sample with lead acetate solution and excess of sodium hydroxide, when black lead sulphide will separate.

For the detection of iso-thiocyanates or thiocarbimides, such as exist in oil of mustard, the sample should be boiled with alcoholic sodium hydroxide, the solution diluted with water, acidified with hydrochloric acid, and a drop of ferric chloride added. The production of a blood-red colour, due to the formation of ferric thiocyanate, indicates the previous existence of an isothiocyanate (thiocarbimide).

Methods for the estimation of sulphur compounds in essential oils are fully described under Oil of Mustard (Vol. 7).

General Plan of Analysis.—As a rule, the problem with which the analyst is confronted is not to deal with a totally unknown type of essential oil, but to decide on the purity and value of an oil of a known type. This being the case, any general scheme of analysis must necessarily be modified to meet the given conditions.

The sp. gr. of essential oils varies within comparatively narrow limits in most cases, although in a few the variations are very wide. The determination of this and other physical characters are therefore of the utmost importance; and the figures for the sp. gr., optical rotation, and refractive index will very often suffice to decide whether a given oil is pure or not. In general, the physical characters can be so nicely balanced by a skilled adulterator that it is not difficult to make mixtures having the physical characters of a genuine oil. It is here that the value of fractional distillation comes in. If the oil be distilled, either at ordinary or at reduced pressure as the case may require, and the temperatures of the various fractions noted, and then the physical characters of the fractions taken, it will be found very difficult to imitate such a combination of figures. For example, a pure oil of peppermint, having a refractive index 1.4645, will, on distillation at

reduced pressure, give fractions the refractive indices of which vary from 1.4600 to 1.4660, until the last 10% residue, which will have a refractive index about 1.4780 to 1.4790.   The recent use of triacetin as an adulterant of this oil was detected by the indications afforded by this last 10% of the oil on distillation, when the refractive index was found to be 1.4436, so low as to at once point to adulteration with a substance of low refractive index and high b. p.   Again in the case of another recent adulterant of this oil, the last fractions were found to have refractive indices up to 1.4900 to 1.4980.   This figure at once suggests a substance of the sesquiterpene or phenolic type.   As a matter of fact it was found to be the sesquiterpene oil of African copaiba.   Such considerations demonstrate the necessity of examining the physical characters of the fractions of the oil rather than to place too much reliance on those of the oil itself.

The determination of the physical characters should be followed by the necessary quantitative valuations.   These include (according to the type of oil) the determination of 1. free acids; 2. phenols; 3. alcohols; 4. esters; 5. aldehydes and ketones.   The general principles of these processes will now be described, other processes, necessary in individual cases, being left for detailed treatment under the oils themselves.

Estimation of the Free Acids in Essential Oils.

The acids may be determined rapidly and with considerable accuracy by dissolving a known weight of the essential oil in neutral methylated spirit, adding a few drops of phenolphthaleïn solution, and titrating the liquid with standard alkali hydroxide.   The operation may be carried out exactly as in the case of fixed oils (Vol. 2).

1 c.c. of normal sodium hydroxide requires for neutralisation:

> 0.060 grm. of acetic acid.
> 0.102 grm. of valeric acid.
> 0.122 grm. of benzoic acid.
> 0.148 grm. of cinnamic acid.
> 0.138 grm. of salicylic acid.
> 0.164 grm. of coumaric acid.
> 0.168 grm. of vanillic acid.

Hydrocyanic acid, which is found in bitter-almond oil, cherry-laurel oil, etc., cannot be readily titrated, but may be estimated with accuracy by the methods described in Vol. 7.

Detection and Estimation of Phenols.

The presence of phenols may often be detected by dissolving the sample in alcohol and adding a solution of ferric chloride, which produces a blue or violet colouration. Chavicol, eugenol, and thymol are among the phenols which respond to this test.

Phenols may be extracted from essential oils containing them by agitating the sample with aqueous alkali hydroxide. Any free acids present will be dissolved out with the phenols; hydrocyanic acid and benzoic acids from bitter-almond oil and cinnamic acid from oil of cinnamon being thus extracted. The process may readily be made quantitative by simply agitating a known volume (e. g., 10 c.c.) of the oil with a 5% solution of alkali hydroxide in a graduated tube, or a flask with a narrow neck graduated in divisions of 0.1 c.c., observing the decrease in the volume of the oily layer. It sometimes happens that the oily and aqueous strata do not separate sharply, in which case a definite volume of petroleum spirit may be conveniently added and deducted from the observed result. The foregoing process may be employed for the estimation of thymol in oil of thyme and eugenol in clove oil. This estimation is only approximate, as bodies other than phenols are absorbed to a small extent.

Schryver (*J. Soc. Chem. Ind.*, 1899, **18,** No. 6) proposes to estimate phenols by the use of sodamide, which is decomposed by phenols, with the separation of ammonia. As water also decomposes the amide, it is necessary to be sure that the sample examined is dry. His process is as follows:

About 1 grm. sodamide is reduced to a fine powder, washed by decanting it 2 or 3 times with a little benzene, and placed in a wide-mouthed flask of 200 c.c. capacity, connected with a separating funnel and an inverted condenser. From 50 to 60 c.c. of thiophene-free benzene is placed in this flask, and brought to boiling on a water-bath, a current of air freed from carbon dioxide being at the same time introduced, by means of a water-air pump, through the separating-funnel, which dips under the surface of the liquid. Ten minutes' boiling will remove the last traces of ammonia which may·have adhered to the sodamide. About 20 c.c. of normal sulphuric acid are then placed in the ammonia absorption bottle. A solution of between 1 and 2 grm. of the phenol or essential oil under examination is then slowly added through the separating funnel to the boiling

mixture of sodamide and benzene, the funnel washed with a little benzene, and air aspirated through the boiling contents of the apparatus, until all the ammonia in the receiver has been absorbed. This usually takes about 75 minutes. The excess of sulphuric acid in the receiver is then titrated with normal sodium carbonate, methyl-orange being employed as indicator. The result is expressed either in percentages of phenol or (especially in the case of unknown oils) by the "hydroxyl value," by which Schryver means the number of c.c. of normal sulphuric acid required to neutralise the ammonia generated, under the above conditions, from 1 grm. of the material. (For further details see Vol. 3, under *Phenols*.) .

Estimation of Alcohols in Essential Oils.

Many essential oils contain free alcohols, often to so great an extent as to owe practically the whole of their odorous characters to them. Sandalwood, peppermint, rose, and geranium are types of oils rich in free alcohols.

No practicable method of actually separating these alcoholic substances exists, and their estimation must be regarded as approximate. So long as the estimation is carried out with care and under uniform conditions, however, the results are strictly comparable, when the following process is employed. The alcohols in the oil are converted into acetic esters, and a known weight of the acetylated oil is saponified by a solution of potassium hydroxide in alcohol. The actual estimation made is, of course, the amount of potassium hydroxide used for the saponification. From this the amount of a given alcohol can easily be calculated; it is therefore necessary to calculate the amount of free alcohols in terms of the predominating one present, such, for example, as geraniol in geranium oil. Although it is true that, in general, the free alcohols in an essential oil consist of a mixture of more than one compound, these are usually of nearly the same formula, so that a calculation in terms of one of them is approximately true for them all. It is obvious that no estimation of a mixture of geraniol, $C_{10}H_{18}O$, and a sesquiterpene alcohol could afford any basis for an accurate calculation.

Before describing the process usually adopted, it is necessary to point out that certain other substances react with acetic anhydride, and

yield saponifiable esters. Such, for example, is citronellal, which is
converted into isopulegyl acetate by acetylation; so that the amount
of "free alcohols" as determined by acetylation in citronella oil, in
reality represents both the alcohols and the citronellal. Again, certain
alcohols are partially decomposed during the process, and the results
obtained are far below the truth. Such are the alcohols' terpineol and
linalol. In order to obviate this difficulty, Boulez recommends dilut-
ing the oil containing such alcohols with 5 times its weight of pure
turpentine, and acetylating with about 8 times its weight of acetic
anhydride. A blank experiment with only the oil omitted is necessary,
and the proper deduction can thus be made. Although this does not
give quite accurate results, the dilution is a distinct advantage, and the
results are not very far below the truth.

For normal cases, 10 to 20 c.c. of the sample are mixed with an
equal volume of acetic anhydride and about 2 grm. of sodium acetate
(anhydrous). The last-named is added to absorb the water liberated
by the action, which would otherwise have a reversing effect on the
esterification. The mixture is boiled in a glass flask, having a tube
about 4 feet in length ground into its neck, during 2 hours. The high
b. p. of acetic anhydride renders the glass tube an efficient condenser,
and water condensation is not necessary. When the mixture is cold,
it is well shaken with twice its volume of water in a separator, and when
the layers have separated the water is run off. This is repeated 4
times or until the water contains no acetic acid. The acetylated oil
is now allowed to stand for a short time on a little anhydrous potassium
hydrogen sulphate to remove traces of water, and, if necessary, filtered.
For oils usually containing 70% or more of alcohols, about 2 grm. are
used for saponification, while with oils containing only 15 to 20%,
up to 5 grm. may be used. The acetylated oil, accurately weighed, is
now boiled briskly with 20 to 25 c.c. of $N/2$ alcoholic potassium
hydroxide under a reflux condenser for $1/2$ hour, and the amount of
alkali used is determined in the usual manner by titration with $N/2$
acid.

Assuming that the original oil contains no esters or at most a negli-
gible quantity, the calculations are simple enough, as the whole of the
alkali used is employed for the saponification of the esters formed by
the acetylation of the free alcohols. Remembering that the oil used
for the saponification represents a smaller amount of the original oil,
on account of its combination with the acetyl radical, the following

◦ formula will (in the case of ester-free oils) give the amount of free alcohols present:

$$P = \frac{M \times N}{10 \; (W - 0.042 \; N)}$$

where P is the percentage of alcohol present, M is its molecular weight, and N is the number of c.c. of *normal* alkali used. The correction 0.042 N is for the increase in weight of the oil due to acetylation. If the oil originally contains both esters and alcohols these calculations will be useless. In such cases it is necessary to proceed as follows:

1. Estimate the amount of combined alcohols by a preliminary saponification of the esters.   ◦

2. Saponify about 20 grm. of the sample with alcoholic potassium hydroxide solution, add water, and well wash the separated oil, now free from esters, dry over potassium hydrogen sulphate, and

3. Estimate the total alcohols (which are now all free) in 2 to 5 grm. of 2.

4. The amount of alcohols found in 3 refers, not to the original oil, but to the saponified sample; to calculate the total alcohols in the original sample a correction must be made by allowing for the reduction in weight by saponification of the original oil. This reduction can be ascertained by calculation from the amount of alkali used for saponification in 1.

5. Deduct the combined alcohols found in 1 from the total alcohols found in 4. This gives the amount of free alcohols.

It is assumed that the esters are uniform in molecular weight, usually as acetic esters. This is not always accurate, as, for example, in peppermint oil where some of the esters are those of valeric acid. But the results are sufficiently accurate for all ordinary purposes. In some oils the esters are principally those of higher acids; for example, in geranium oil where they are calculated to tiglic acid.

Power and Kleber (*Zeit. Anal. Chem.*, 1894, **33**, 762), in describing the determination of menthol in peppermint oil, give the following formula for calculation:

$$P = \frac{a \times 15.6}{s - (a \times 0.042)}$$

where P is the percentage of menthol (total), s is the weight in grm. of the oil which has first been saponfied and then acetylated, and a is the number of c.c. of *normal* alkali used.

But an examination of this formula shows that P is, in fact, calculated, on the weight of the ester-free oil, and for strict accuracy requires the slight correction referred to above (No. 4).

Haller recommends the following modification of the above process in the examination of the oils of geranium, citronella, peppermint, etc.: The amount of esters is first separately estimated, and then a separate portion of the oil is saponified with a suitable amount of potassium hydroxide, so as to obtain the whole of the alcohols in a free state. The product is separated from the aqueous liquid, washed with water, and dried with anhydrous sodium sulphate. The dried liquid is then heated either with succinic or phthalic anhydride, whereby the alcohols are converted into mono-ester acids. Strong sodium hydroxide solution is then added to convert these compounds into sodium salts, and the terpenes and other indifferent substances are then removed by agitation with ether. The pure alcohols are recovered by saponifying the alkaline liquid and extracting with ether.

Estimation of Esters in Essential Oils.

Esters in essential oils may be readily estimated by the saponification process of Koettstorfer employed for the examination of fixed oils (see Vol. 2). Certain modifications of the procedure there prescribed are sometimes desirable, such as judicious alterations in the quantity of the sample and in the strength of the alkali used.

In certain cases, essential oils contain a small quantity of free acids, when, of course, a preliminary titration with $N/2$ alcoholic potassium hydroxide will be necessary, and a due allowance made for the acids. Esters such as linalyl acetate (in lavender and bergamot oils), geranyl tiglate (in geranium oil) frequently form the most important constituents of essential oils. While different views are held as to the direct proportion between ester content and odour value in certain oils, such, for example, as lavender oil, in other cases it is quite certain that the odour value is in practically direct ratio to the ester value. This is true in the case of bergamot oil, which owes its perfume to the linalyl acetate present. Indeed, it may be accepted that where the ester is associated with no other compound of much odour value this holds good, but where, as in the case of lavender oil, there are numerous other substances contributing to the odour of the oil, the ratio between ester content and odour value is not direct.

Saponification of from 2 to 5 grm. of the oil under a reflux condenser

·for half an hour, by boiling with 15 to 25 c.c. of alcoholic potassium hydroxide of approximately $N/2$ strength, and titration of the excess of alkali with $N/2$ sulphuric acid at once gives the percentage of esters, assuming that only 1 ester is present. As a matter of fact, usually there are several esters present, often of different molecular weights, so that in practice the amount of alkali consumed is calculated to the predominant ester, such as menthyl acetate in peppermint oil, linalyl acetate in bergamot and lavender oils, and geranyl tiglate in geranium oil.

Thus 1 c.c. of normal alkali hydroxide represents:

> 0.088 grm. of ethyl acetate.
> 0.152 grm. of methyl salicylate.
> 0.196 grm. of linalyl acetate.
> 0.196 grm. of bornyl acetate.
> 0.198 grm. of menthyl acetate.

Estimation of Aldehydes and Ketones.

Certain essential oils, as, for instance, the oils of bitter almonds, cassia, cinnamon, citronella, and lemon-grass, are chiefly or largely composed of aldehydes. These may be detected by most of the general tests for aldehydes (Vol. 1), and may conveniently be estimated by converting them into their bisulphite compounds.

The method usually adopted for the estimation of aldehydes and ketones which form bisulphite compounds is some variation of the original absorption process with a hot saturated solution of sodium hydrogen sulphite. It must be remembered that all absorption processes are merely approximate owing to the slight solubility of the constituents which are called non-absorbable, and the incomplete absorption which may happen with the absorbable compounds.

Oils such as cassia and lemon-grass are those upon which this estimation is most frequently necessary. The estimation of citral in lemon oil is attended with many difficulties, and will require special treatment under "Citral" (see p. 270).

The condition requisite for an accurate estimation is that the non-absorbable layer of oil should separate sharply from the absorption liquid without any waxy or flocculent substances to interfere with a correct reading.

The absorption is carried out in a Hirschsohn flask a flask holding

about 150–200 c.c., and having a long neck graduated to 10 c.c. in 0.1 c.c.   5 or 10 c.c. of the oil are introduced into the flask, and a hot 30–40% solution of sodium hydrogen sulphite added to about 1/3 of the capacity of the flask.   In the case of cassia oil, the absorption is facilitated by standing the flask with the oil in it in the water-bath for 5 minutes before adding the solution.   The 'whole is well shaken, care being taken that none of the crystals formed get into the neck of the flask, as they often remain firmly attached there and render the absorption very tedious.   The flask is now placed in boiling water, and shaken from time to time with the addition of more sulphite solution.   This is continued until the whole of the crystals are ab-sorbed, and nothing but a clear oily layer floats on the surface.   More solution is carefully run in, until the oily layer is forced up into the neck.   The flask is allowed to stand for 4 hours at least and then the non-absorbed layer is read off, the difference being taken as aldehyde or ketone.   The separation of the non-absorbable layer by means of ether, with subsequent removal of the ether and weighing the oil has been suggested, but this method has no advantage over the other, and is far more tedious.   Burgess (*Analyst*, 1904, **29**, 78) has exam-ined the various processes for the estimation of aldehydes and ketones, and his results may be summarised as follows (see also under Citral, p. 270):

1. By the use of sodium hydrogen sulphite (as just described). He objects to the time required, and the frequent separation of resinous matter which renders the reading of the meniscus at the time of separation difficult.   This is, however, as pointed out above, only true in certain cases.

2. By condensation with cyanacetic acid in the presence of potassium hydroxide.   He considers that absorption with this reagent always gives too high results.   The reagent was first suggested by Tiemann, and afterward recommended by E. J. Parry, who, however, has since shown that an absolutely fresh specimen of cyanacetic acid is necessary to obtain results which approximate to the truth.   In practice this method is rarely used.

3. Absorbing the oil by a saturated solution of sodium salicylate. It is clear that sodium salicylate forms compounds with many oxygen-ated compounds in essential oils, but probably substances other than aldehydes and ketones are absorbed, and the method has been discarded.

4. The hydroxylamine method. This method depends on the fact that many aldehydes and ketones form oximes when acted on by excess of hydroxylamine in alcoholic solution. The amount of unused hydroxylamine is estimated by titration, and from the amount that has entered into combination, the amount of aldehyde or ketone is deduced. *This method appears to have some advantages in the case of oils containing a small amount of aldehyde, but some difficulty is usually experienced in deciding upon the end point of the titration. It is, in practice, only used for the estimation of citral in lemon oil, and will therefore be described at length under that oil (see p. 270). Burgess states that the conditions of this estimation vary with different oils, and that no definite instructions can be prescribed which will apply to all oils.

5. By the use of semioxamizide. Hanus has recommended the use of this substance (*Pharm. Cent.*, 1904, 37). It is only suggested for the estimation of cinnamaldehyde in cassia and cinnamon oils, and will be found described in detail under "Cassia" (Vol. 3).

6. By the use of a neutral solution of sodium sulphite. This is the method which Burgess prefers, and is applicable to a very large number of essential oils.

The oil (5 to 10 c.c.) is absorbed, as in the case with sodium hydrogen sulphite, in a Hirschsohn flask, with a saturated solution of neutral sodium sulphite, a soluble sulphonate being formed. In the case of citral, for example, the following reaction takes place:

$$C_9H_{15}CHO + 2Na_2SO_3 + 2H_2O = C_9H_{17} (NaSO_3)CH.OH.SO_3Na + 3NaOH.$$
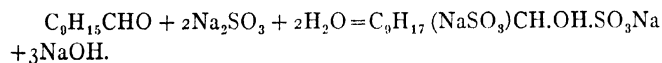
The flask containing the mixture is heated on a water-bath, 2 or 3 drops of phenolphthaleïn being added. As combination proceeds, alkali is liberated and a red colour is developed. This is discharged by the careful addition of 10% acetic acid, the mixture being so kept neutral until no further liberation of alkali is observed. The unabsorbed oil is then forced by the addition of further sulphite solution into the neck, and after due time for all the globules of oil to separate, the oil layer is read. By this method good results may be obtained in the case of the following oils: bitter almond, caraway, cassia, cinnamon, citral-containing oils, citronella (if heated for a very long time), cumin (litmus is the better indicator, with this oil), pennyroyal (litmus is the better indicator), spearmint.

In oils containing only a small amount of aldehydes, such as lemon oil, this method does not succeed, as the reading of the meniscus is obscured by the presence of some flocculent matter.

Schimmel and Co. (*Bericht*, November, 1908, 83), states that, in the case of lemon-grass oil, sodium sulphite acts only on the citral, whereas the hydrogen sulphite reacts with part, at least, of the methyl-heptenone. Hence different results are obtained by the two processes.

A result of 2 to 5.5% higher is thus obtained by the use of the hydrogen sulphite than with the neutral sulphite process which gives more accurate results. At the same time the acid sulphite method is the process almost universally employed with this oil, and therefore it is necessary to state the process used in comparing results obtained.

Bruylants (*Bull. Acad.*, R. Belg., 1907, 11, 955) has published a method for the estimation of aldehydes, especially as applied to oil of lemon.

It is based on the fact that after adding ammonium sulphide to defibrinated blood in the presence of a small quantity of aldehyde, the two absorption lines of oxyhæmoglobin diminish in intensity until a third line appears between them, which becomes more and more distinct, and finally becomes as intense as the other lines. The following instruments and reagents are required to carry out the method: a spectrophotometer, the field of view of which, for the purpose of comparative observations, is divided into 2 superincumbent equal parts, and the necessary vessels for holding the solutions, burettes, and test-tubes; a 3% blood-solution prepared from fresh defibrinated pig's blood which in the spectroscope shows the two characteristic lines of oxyhæmoglobin; a solution of ammonium sulphide, which must be prepared with particular care in order to obtain the desired effect (a definite volume of ammonia is saturated with hydrogen sulphide gas, mixed with a slightly larger volume of ammonia, and the ammoniacal sulphide thus obtained exposed to the light for a few days); citral solutions with 3, 4, and 5% citral in citral-free oil (for comparison), and finally 94% alcohol, freed from aldehyde by boiling with potassium hydroxide and metaphenylene-diamine hydrochloride.

Before the estimation is carried out, preliminary tests must be made so as to obtain an approximate aldehyde content. Samples of 9 c.c. of the blood solution are mixed under exactly the same conditions with 1 c.c. ammonium sulphide solution each, and then, without shaking, the solution of the oil under examination, or the 5% comparison citral solution

at the same time slowly poured on the top. Both solutions are pre-
pared in the proportion of 5 c.c. alcohol to 1 c.c. of the aldehyde-
containing oil. First of all 0.15 c.c. of such solution are added.
Next, the vessels are shaken for about half a minute. After separating
the insoluble portions, the lower layer is removed by means of a pipette,
and placed in the vessel of the spectroscope. If the work is done
sufficiently quickly, it is possible to determine first of all the ab-
sorption lines of oxyhæmoglobin in both parts of the field of view;
next the line in the middle appears as the first phase of the reaction,
and it does so in both parts simultaneously if the aldehyde quantities
in the two solutions are absolutely equal. If this is not the case, the
quantity of the alcoholic solution of the oil is increased or diminished
by hundredth parts of a c.c., while the quantity of the test-solu-
tion remains unchanged. After 5 or 6 tests the aldehyde content
can thus be approximately estimated. In the exact determination
which now follows, the work is carried on with a comparative solution
of which the aldehyde content approaches as closely as possible that
of the oil under examination. If the oil contains less than 5% of
aldehydes, a commencement should be made with a comparison
solution containing 3 or 4% of citral—if more than 5% of aldehyde,
the 5% solution is employed, and the work is discontinued, exactly as
before, when the central absorption lines appear simultaneously.
After some practice, a complete determination can easily be carried
out in half an hour. The results are very exact.

The following methods are mainly of theoretical interest, and are
rarely employed except in research work.

Aldehydes and ketones may also be isolated by converting them
into the corresponding *semicarbazones* by reaction with semicarbazide.[1]

A solution of semicarbazide is conveniently prepared in accordance
with the directions of Thiele and Stange (*Annalen*, 1894, **281**, 19) by
dissolving together 130 parts of hydrazine sulphate, 55 of sodium car-
bonate, and 85 of sodium cyanate in 1,000 parts of water. 100 c.c. of
this solution is treated with 150 c.c. of alcohol, and the liquid filtered
after standing for several hours. A weight of 10 grm. of the aldehyde
to be tested is then added to the clear filtrate. The semicarbazone
crystallises out gradually and the greater part separates in the course

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[1] *Semicarbazide*, or carbamic hydrazide, $NH_2.CO.NH.NH_2$, may be prepared by heating
a mixture of molecular proportions of urea and hydrazine hydrate for 3 hours in a sealed
tube at 100°. It crystallises in colourless prisms melting at 96°, and reduces Fehling's
solution and ammoniacal silver nitrate in the cold. When shaken with aldehydes, semi-
carbazide yields characteristic crystalline compounds (semicarbazones).

of 24 hours. The liquid is then filtered and the semicarbazone still in solution precipitated by addition of water and recrystallised from alcohol. The united products are then purified by solution in methyl alcohol and precipitation by water.

Carbonyl Number. •

Benedikt and Strache (*Monatsh.*, 1893, **14**, 270) have proposed to estimate the total amount of *ketones* and *aldehydes* present in an essential oil by ascertaining the carbonyl number or yield of *hydrazone* obtained by treating an alcoholic solution of the sample with phenyl-hydrazine hydrochloride and sodium acetate, used in quantity roughly proportionate to the aldehydic and ketonic substances present. If the carbonyl number is above 40, from 0.5 to 1.2 grm. of the substance is treated with a weight of phenylhydrazine hydrochloride between 1 and 1.5 times the weight of the oil. With a carbonyl number between 10 and 40, from 1 to 2 grm. of substance should be employed with from 0.5 to 1 grm. of the reagent. When the carbonyl number is below 10, from 2 to 5 grm. of the sample and 0.5 grm. of the reagent should be used. In any case a quantity of sodium acetate is added equal to 1.5 times the weight of phenylhydrazine hydrochloride employed, and preferably in 10% alcoholic solution. The mixture is warmed on the water-bath for a quarter of an hour in a flask holding about 100 c.c., and filled about two-thirds with the alcoholic fluid, whereby too vigorous ebullition is avoided; after cooling, the liquid is diluted to 100 c.c. with water, the insoluble matter filtered off through a dry filter, and 50 c.c. of the filtrate oxidised with Fehling's solution. The nitrogen thereby evolved is collected and measured, so as to ascertain the amount of unaltered phenylhydrazine in the liquid, and thus obtain the data for determining the quantity precipitated as hydrazone. For this purpose a standard solution of phenylhydrazine may be conveniently used in the first instance, containing about 5%, its precise strength being determined by treating a known volume with Fehling's solution. The salt must
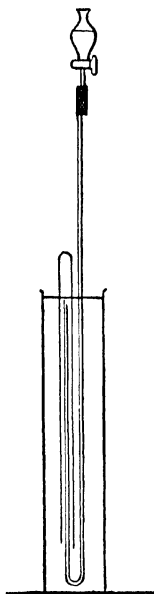
FIG. 3.

be free from aniline. The purification of the nitrogen from benzene vapour is necessary when accurate results are desired, and is effected by Benedikt and Strache by the arrangement shown in Fig. 3. The longer end of the U-tube is fixed to a stoppered reservoir, the shorter end being drawn out to a fine point and placed inside the tube containing the nitrogen to be purified. About 200 c.c. of alcohol is now allowed to run down from the reservoir so as to spurt upward in a fine jet into the nitrogen tube; this absorbs all benzene vapour present in the nitrogen. In turn, some 400 c.c. of water is similarly passed down from the reservoir to absorb alcohol vapour, after which the measuring tube is removed to another vessel containing water, and the volume of the nitrogen read off. A number of direct observations with nitrogen, to which benzene was added after measurement, showed that this method of treatment sufficed to remove all benzene vapour within the limits of reading-error.

A Lunge's nitrometer can be conveniently substituted for the above arrangement.

Duplicate determinations made in this way are stated rarely to differ more than at most 1 or 2 units in the value of the carbonyl number deduced, but this value sometimes exhibits a considerable divergence from the actual amount of aldehyde or ketone present. The following figures were obtained with different samples of oils containing large proportions of aldehydic or ketonic constituents:

Oil, etc.	Carbonyl number	Aldehyde or ketone present	% of aldehyde or ketone
Cumin...	51.8	Cuminal, $C_{10}H_{12}O$	47.9
Cumin...	45.2	Cuminal, $C_{10}H_{12}O$.	41.8
Cumin..	96.7	Cuminal, $C_{10}H_{12}O$.	89.4
Caraway.	42.0	Carvone, $C_{10}H_{14}O$.	39.3
Caraway.	33.6	Carvone, $C_{10}H_{14}O$....	31.5
Caraway.	38.3	Carvone, $C_{10}H_{14}O$.	35.9
Caraway.	61.1	Carvone, $C_{10}H_{14}O$..	57.3
"Carvol".	84.0	Carvone, $C_{10}H_{14}O$.	78.8
Bitter-almond.	147.5	Benzaldehyde, C_7H_6O.	97.7
Bitter-almond, free from hydrocyanic acid.	147.7	Benzaldehyde, C_7H_6O.	97.7
Bitter-almond, artificial.	145.3	Benzaldehyde, C_7H_6O.	96.2
Cinnamon	92.7	Cinnamic aldehyde, C_9H_8O'.	76.5
Cinnamon	77.4	Cinnamic aldehyde, C_9H_8O..	63.9
Cassia	94.3	Cinnamic aldehyde, C_9H_8O..	77.8
Cassia	79.9	Cinnamic aldehyde, C_9H_8O..	66.0

For the preparation of the condensation products of aldehydes (e. g., geranial) with acetone, in such a manner as to avoid secondary reactions, W. Stiehl recommends the following mode of operating:

A weight of 50 grm. of the well-dried and freshly distilled aldehyde is dissolved in 50 c.c. of absolutely dry acetone, and the solution cooled down to 0° at least. A weight of 2.5 grm. of sodium is dissolved in 50 c.c. of strictly absolute alcohol, and the solution also cooled down to 0°. Finally, 10 grm. of tartaric acid is dissolved in 50 c.c. of water. The solution of sodium ethoxide is then added to the solution of the aldehyde in acetone, the mixture being kept cool and continually stirred, and in 15 minutes the action is interrupted by the addition of the solution of tartaric acid. The acetone and alcohol are then distilled off in a current of steam, and the residual oil is separated from the solution of tartaric acid and washed. The oil thus obtained is distilled with superheated steam and then rectified either under diminished pressure or purified by means of a solution of sodium hydrogen sulphite. For this purpose a 50 grm. portion of the crude acetone condensation product is boiled with 100 c.c. of commercial solution of sodium bisulphite, and 100 c.c. of water, for about 3 hours under a reflux condenser. After the whole is cooled down the small quantities of substances which are not ketones are carefully removed by agitation with ether, and the sulphite compound decomposed in the cold with sodium hydroxide. The separated oil is well washed, and rectified, first with superheated steam and then under diminished pressure.

O. Doebner (Ber., 1894, 27, 252 and 2020) has described a reaction which appears to be strictly characteristic of the aldehydes, and does not take place with other compounds containing a CO— group, such as ketones, lactones, and dibasic acids.[1] The test is applied by treating the aldehyde with molecular proportions of pyroracemic acid (pyruvic acid) and β-naphthylamine, when a crystalline compound is formed having the constitution of an α-alkyl-β-naphthocinchoninic acid. The reaction is applied by Doebner to the detection of citral and citronellal (see pages 269 and 270).

[1] Doebner's reaction occurs in every case tried except that of hydroxyaldehydes, such as glycerose, in which a hydroxyl-group is linked to the carbon atom to which the aldehydic residue is attached. Doebner considers this an explanation of the fact that sugars which are regarded as having an aldehydic constitution do not respond to the test.

The Iodine Value of Essential Oils.

In the last edition of this volume considerable space was devoted to this determination. In the ordinary way it would now be dismissed in a few lines, but as several papers have from time to time been published laying stress on the value of the iodine number as determined by Hübl's process, it is necessary to draw attention to the fact that in most cases the determination is useless.

The only reason that this process has been applied to essential oils is because the word "oils" is common to them and to the group of substances classed as fatty oils. These latter are all in close chemical relationship, and the various members are very constant in character. For a process to be applicable to a group of compounds, it is obvious that the reactions taking place in that process should be the same, or nearly the same in all the members of that class of bodies. This is true in the case of the fatty oils, where one has simply to consider the amount of addition—with possibly some substitution—of iodine to, or in, the molecule of fatty acid. In fact the iodine process is to be regarded as a measure of the amount of unsaturated fatty acids. To apply it to essential oils is to distort its purposes and value almost to an absurd point. The papers of Barenthein, Davis, Snow, Williams, and Cripps on this subject need only to be examined together to cause the process to be left severely alone as applied to essential oils. These substances, in the first place, consist of such widely different classes of compounds, that the reactions taking place are different in almost every group. Hence the iodine value ceases to have the precise meaning that it has in the case of fatty oils. Secondly, with many of the compounds found in essential oils, the reactions are so energetic that it is impossible to control them quantitatively. Thirdly, the reactions are such that the slightest variation in temperature, exposure to light, time of reaction, and—which is most important—the excess of iodine used over that which can possibly enter into action, so influence the result that the same worker can but rarely obtain concordant values with the same sample.

It is true that there are cases where these conditions are not accentuated and where fairly constant results can be obtained. These are, however, but few, and the process is not worth serious consideration in regard to this group of substances. A few examples of the unreliability of the iodine-value may here be given.

Aniseed oil is one which varies but little, and its composition is such that, if there were any theoretical quantitative reaction possible by this process, it would be very constant. The values recorded by Barenthein, Davis, and Shaw, respectively, are 164, 190, and 121. Clove oil is one which contains usually between 80 and 90% of eugenol, the remainder consisting mainly of one or more sesquiterpenes. In spite of this not very wide variation in composition, the same 3 observers give 270, 349–367, and 467.

Again Williams, on 2 samples of aniseed oil found 274 and 186, a difference that can never be shown to have any ratio to the difference in composition. In practice to-day no chemist used to examining essential oils employs this very unreliable process.

Methoxyl Numbers of Essential Oils.

The determination of the proportion of methyl or equivalent alkyl radical eliminated from the molecule by treatment with hydriodic acid, was proposed by S. Zeisel in 1886 as a method of differentiating essential oils. The process consists in heating the compound with concentrated hydriodic acid, and receiving the alkyl iodide formed in an alcoholic solution of silver nitrate. From the weight of silver iodide produced that of the alkyl radical (in terms of methyl or methoxyl) can be calculated, since AgI corresponds to CH_3 O. Zeisel's method has been somewhat modified by Benedikt and Grüssner (*Chem. Zeit.*, 1889, **13**, 872) who operate as follows: From 0.2 to 0.3 grm. of the substance is placed in a flask of 30 to 35 c.c. capacity, and treated with 10 c.c. of hydriodic acid of 1.70 sp. gr.[1] The flask is heated in a bath of glycerin, a current of carbon dioxide being passed through it.[2] The alkyl iodide formed passes through a series of bulbs, the first of which is empty, the second contains water, while the third contains water holding purified red phosphorus in suspension.[3] The bulbs are sur-

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[1] Herzig makes an addition of 8% of acetic acid to the hydriodic acid (*Monatsh.*, 1888, **9**, 544). The hydriodic acid employed should be free from sulphur and phosphorus compounds and should be tested by means of a blank experiment.

[2] W. H. Perkin (*Trans.*, 1903, **83**, 1367) employs a special form of long-necked distilling flask designed to prevent hydriodic acid from distilling over with the alkyl iodide, the latter being absorbed by impinging on the surface of the liquid in the first flask and by bubbling the gases through the liquid in the second flask.

[3] G. Gregor replaces the red phosphorus and water in the third bulb by a solution of 1 part of arsenious oxide and 1 of potassium carbonate in 10 parts of water. According to W. Kropatschek, the solution of these substances should not be stronger than 1 and 2%. The bulb is liable to become choked with the precipitated arsenious oxide unless refilled for each determination. Not the slightest reduction of the silver nitrate solution in the flask takes place, as in the case when the bulb contains phosphorus.

rounded with water, the temperature of which can be kept, if desired, at 70°; (which is necessary in the determination of ethoxyl, C_2H_5O). After passing the bulbs, the alkyl iodide, which is quite free from hydriodic acid and iodine, is absorbed in a flask containing 5 c.c. of a 40% aqueous solution of silver nitrate and 50 c.c. of 95% alcohol. As a precaution, the gas is further passed through a mixture of 1 c.c. of the silver solution with 10 c.c. of alcohol. The mixed silver solutions are diluted with water, acidified with nitric acid, and the silver iodide filtered off and weighed.[1] By multiplying the weight found by the factor 0.132 $(= \frac{31}{235})$, the equivalent of methoxyl (CH_3O) may be found.

Instead of weighing the silver iodide, G. Gregor (*J. Soc. Chem. Ind.*, 1898, **7**, 609) absorbs the alkyl iodide in a solution of silver nitrate of known strength, and subsequently ascertains the excess of silver in the filtered liquid.

The above methods are evidently inapplicable in the presence of alcohol, but may, on the other hand, be employed for the estimation of alcohol when the true methoxyl number of the oil is known. Absolute alcohol has the methoxyl number 674 $\left(\dfrac{31 \times 1000}{46} = 674 \right)$.

Herzig and Meyer have proposed to differentiate between the methyl radical when attached to oxygen (methoxyl), and when attached to nitrogen (methylimine). They find that, by a suitable modification of Zeisel's process, boiling hydriodic acid liberates the methyl-radical from methoxyl only, while a temperature of 200° to 300° is required for the hydrolysis of the methylimine radical.   M. Busch, however (*Ber.*, 1902, **35**, 1565), states that the decomposition of the methylimine radical occasionally occurs when the compound containing it is simply boiled with hydriodic acid.   Thus if a negative result be obtained with any compound when boiled with hydriodic acid, the absence of methoxyl may be regarded as proved, but a positive result should not be accepted as conclusive evidence of its presence.

In the case of oils containing esters of higher alkyl radicals, such as butyl, amyl, and hexyl, the liquid above the silver precipitate does not become clear even if the treatment with hydriodic acid be continued

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[1] In the presence of sulphur compounds, a black precipitate is formed in the silver solution, and it is necessary to determine the actual weight of iodine precipitated, instead of merely weighing the precipitate.   Or the precipitate may be treated with dilute nitric acid till the silver sulphide is dissolved.   A modified process for the determination of the methoxyl group in compounds containing sulphur has been proposed by F. Kaufler, *Analyst*, 1902, 126.

for many hours, since small quantities of alkyl iodides are continually passing over.

Name of oil	Origin	Meth-oxyl No.	Name of oil	Origin	Meth-oxyl No.
Anise.........	Schimmel & Co.	171.1	Cinnamon-leaf .	....	151.3
Birchwood tar.	....	46.3	Elemi.........	Schimmel & Co.	25.0
Cumin........	....	17.2	Gaultheria.....	Artificial winter-	184.8
Cumin (extra strong)	....	13.6		green oil. Schim-mel & Co.	
Clove ("Euge-nol")	Schimmel & Co.	185.5	Olibanum......	Schimmel & Co's. frankincense oil	18.8
Clove.........	....	152.5	Parsley seed....	Schimmel & Co.	190.5

The above table gives the recorded methoxyl numbers, or milligrm. of alkyl in terms of methoxyl, present in one grm. of various oils. The majority of essential oils, however, contain no alkoxyl radical, and hence give mere traces or no silver iodide when submitted to the process. Among these oils are those of absinthe, bergamot, bitter almonds (both natural and artificial), angelica, orange flowers, copaiba, coriander, cubebs, *Eucalyptus globulus*, Spanish, French, and African oils of geranium, juniper berries, cherry laurel, lavender, balm mint, lemon, peppermint, rosemary, sage, sandalwood, turpentine, and valerian.

The results of the examination of different samples of the same kind of oil did not invariably give the same results. Thus two samples of cumin oil gave small methyl numbers, while two others gave wholly negative results. Similar differences were observed in the cases of the oils of bergamot and citron-peel.

Benedikt and Grüssner point out that the method may be employed for the estimation of the eugenol in the oil of cloves, cinnamon, etc., and of anethole in the oils of anise and fennel. 235 parts of silver iodide precipitated correspond to 164 of eugenol, or 148 of anethole. It must be remembered, however, that such results include small quantities of other substances present containing methyl groups.

Optical Activity of Essential Oils.

The great majority of natural essential oils exercise a rotatory power on the plane of polarisation of light, and the optical activity may be ascertained quantitatively by the use of a polarimeter. The instrument employed should be one in which monochromatic light is used, saccharimeters constructed for observing the transition

tint not being suitable for the purpose. The result of the observation commonly recorded is the angle of rotation observed when a column of oil 1 decimetre in length is traversed by the light. This may be conveniently called the "optical activity" of the oil. Sometimes this observation is calculated to the "specific rotatory power" of the sample by dividing the angle of rotation by the sp. gr. of the oil. Not a little confusion has arisen through observers' failing to state distinctly on what basis their results are expressed. In this volume all values for optical rotation are to be taken as referring to 100 mm. (1 decimetre) of the substance, unless otherwise specified. Optical activity may be denoted by the symbol [α], the specific rotatory power being expressed as [α]$_D$.

The optical activity of an essential oil is one of the most valuable factors in its examination for purity, and this value is accentuated by optical observations on the fractions separated by distillation. Further, an observation of the optical activity of certain of the constituents of essential oils is a valuable criterion of the purity of the substances in question.

Refractive Indices of Essential Oils.

The determination of the refractive indices of essential oils is of considerable value in certain cases, but the figures given by a genuine oil and its adulterants frequently overlap each other to such an extent as to render the factor of little or no use. Still there are many instances in which the sp. gr. and optical activity of an essential oil differ little from those of its common adulterants, and in these cases the determination of the refractive index will often give valuable information. Thus, oil of wintergreen has a high and nearly constant refractive index of about 1.5370 at 20°. Almost any adulterant will be directly detected by the determination of the refractive index of the sample. Sandalwood oil has also a high refractive index (about 1.5050 at 20°), and although adulteration with cedar-wood oil (refractive index, 1.500) could not be recognised by this method, the addition of castor oil would be readily detected.

Other useful applications of the determination will be made when its value is more generally recognised. The observation of the refractive index of the successive fractions yielded by a complex oil on distillation (preferably under reduced pressure), gives much sharper and more

REFRACTIVE INDICES OF ESSENTIAL OILS (PARRY).

Oils	Sp. gr. at 15°	Optical rotation in 100 mm. tube	Refractive index at 20°
Aniseed	0.985	−1.0	1.5541
Aniseed	0.987	−0.7	1.5545
Bergamot			1.4650–1.4688
Cardamom			1.4661
Caraway			1.4870–1.4950
Cassia			1.5851–1.600
Cedar-wood	0.948	−35.0	1.5011
Cedar-wood	0.947	−33.5	1.5004
Citronella	0.906	−12.0	1.4811
Citronella	0.909	−10.5	1.4830
Clove	1.054	−0.5	1.5306
Clove	1.052	−1.0	1.5310
Clove (90% eugenol)	1.056	−0.7	1.5318
Clove (light)			1.5360
Clove stem			1.5264; 1.5301
Coriander			1.5322
Cumin			1.4994
Eucalyptus (B.P.)	0.917	+2.0	1.5040
Eucalyptus (B.P.)	0.919	−1.5	1.4629
Geranium (French)			1.4662
Geranium (East Indian)			1.4679
Hop			1.4863
Lavender (English)			1.4795–1.4900
Lavender (French)			1.4695; 1.4678
Lemon	0.858	+59.0	1.4638; 1.4643
			1.4754

Oils	Sp. gr. at 15°	Optical rotation in 100 mm. tube	Refractive index at 20°
Lemon	0.859	+58.5	1.4757
Lemon-grass	0.899	+1.0	1.4862
Lemon-grass	0.900	±0.0	1.4855
Lime (hand-pressed)	0.880	+40.0	1.4840
Lime (hand-pressed)	0.878	+35.5	1.4846
Lime (distilled)	0.859	+39.0	1.4760
Lime (distilled)	0.862	+38.5	1.4770
Petitgrain			1.4623
Pimento			1.5309; 1.5303
Rose			1.4619; 1.4609; 1.4615
Rue			1.4614; 1.4621
Spike lavender	0.909	+6.0	1.4341
Spike lavender	0.910	+7.0	1.4670
			1.4666
Constituents.			
Anethole		+0.0	1.5606
Carvone			1.4970
Caryophyllene			1.4999
Cinnamic aldehyde			1.6068
Citral			1.4980
Citronellal		±0.0	1.4481
Citronellol			1.4581
Eucalyptol			1.4582
Eugenol	0.930	±0.0	1.5412
Geraniol			1.4792; 1.4799; 1.4766
Limonene		±63.0	1.4746
Phellandrene			1.4880

definite results than the observation of the index of the untreated sample. Thus, the terpenes have high refractive indices compared with the paraffins and their allies, and the presence of petroleum in essential oils may thus be ascertained. Sesquiterpenes, again, have a very high refractive index, and are thus easily detected in admixture with terpenes. Parry has in this manner recognised the presence of the oil of African copaiba in peppermint oil, and of resin spirit in citronella oil. Glyceryl acetate has also been detected in the residues on fractional distillation of an adulterated oil of peppermint. The very low refractive index at once suggested an open-chain compound.

A number of determinations by E. J. Parry of the refractive indices of certain essential oils and their characteristic constituents are given in the table on page 244. The sp. gr. and optical rotation of many of the samples are also added.

A large number of determinations of the refractive index of various essential oils are recorded in a paper by Utz (*Apoth. Zeit.*, 1901, 742); while H. G. Smith (*Proc. Roy. Soc., N. S. Wales*, 1906, **39**) has recorded the refractive indices of all the known eucalyptus oils (118 species), and based upon the figures obtained a classification of these oils into 7 groups. Such a classification, however, is extremely unscientific.

Adulteration of Essential Oils.

Essential oils are extremely liable to adulteration, the usual sophistications until recently being by addition of oil of turpentine and fixed oils; and by mixing the cheaper essential oils with the more expensive. Scientific methods of adulteration are now largely practised, a type of the methods employed being the case of the addition of ethyl citrate or the acetic esters of glycerin to ester-containing oils, and so on. In addition to the above intentional adulterants, volatile oils are apt to contain water and resinous and other oxygenated bodies produced by their exposure to air.

The proportion of *water* in essential oils is never very large. The hydrocarbons in some cases dissolve about 1:1000, but in the oxygenated oils water is more soluble. The presence of water may be detected by mixing 10 c.c. of the sample of oil, previously filtered if not perfectly clear, with 40 c.c. of petroleum spirit. Any water will be separated in the form of minute globules, which, if in sufficient quantity, will ultimately coalesce and sink to the bottom of the liquid. On adding

a small quantity of plaster of Paris, previously gently ignited and weighed, and agitating thoroughly, the water will be absorbed; and on filtering the liquid through dry paper, washing the plaster with a little anhydrous ether or very volatile petroleum spirit, and drying it at a gentle heat, the increase in its weight will represent the water in the 10 c.c. of the sample of oil employed. The petroleum spirit employed for the above test must be previously dehydrated by agitation with plaster of Paris. ¶

Alcohol in essential oils may be detected by gradually adding some dry powdered calcium chloride, agitating well, and heating in a water-bath between each addition. Mere traces of alcohol render the first portions of the calcium chloride pasty, but if present in larger proportions the salt dissolves and forms a heavy liquid layer. If the experiment be performed in a graduated tube, and a known measure of the oil employed, the diminution in its volume will give that of the alcohol mixed with it. The calcium chloride should be added until it no longer dissolves in the heavier liquid. In testing for small quantities of alcohol by this test, the oil should be previously dehydrated by agitating it with recently ignited plaster of Paris. Dragendorff recommends the use of metallic sodium, which does not act on hydrocarbons, and but slightly in the cold on oxygenated essential oils, if pure and dry; but in presence of 10 or even 5% of alcohol a brisk evolution of gas takes place. Aniline-red (magenta) is insoluble in essential oils, if pure and dry, but in presence of a small proportion of alcohol the oil acquires a pink or red colour. When the proportion of alcohol is considerable, fair quantitative results may be obtained by agitating the oil in a graduated tube with an equal measure of glycerin. The increase in the bulk of the latter liquid, measured after separation is complete, gives that of the alcohol (and water) in the sample examined. Simple agitation of the oil with water removes the alcohol sufficiently accurately for most purposes.

When the actual isolation of the alcohol is desired, E. Barbier recommends that one-tenth should be distilled off and the distillate saturated with an excess of dry potassium acetate, which forms with the alcohol a heavy liquid. This is separated from the layer of oil, mixed with 4 times its volume of water, and again saturated with potassium acetate to get rid of the last traces of oil. The filtered aqueous liquid may then be distilled to one-half, when the alcohol will be found in the distillate.

Chloroform may be detected by dissolving the oil in alcohol and warming the liquid with zinc and dilute sulphuric acid. After some time several volumes of water are added, the aqueous liquid separated from the oil by passing it through a wet filter, and the filtrate tested for chloride by adding silver nitrate and nitric acid. A positive result proves the presence of chloroform in the oil. This substance is, however, rarely used to adulterate essential oils.

The detection and estimation of *alcohol* and *chloroform* in essential oils are rendered more delicate and accurate by previously distilling the sample, and applying the tests to the portion which passes over below 100°. A still better method is to pass a current of steam through the sample of oil contained in a small retort or tubulated flask. Any alcohol or chloroform will be found in the first portions of the distillate. On continuing the operation the essential oils distil over, though their b. p. are considerably above 100°; and after a time little or nothing but *resinous matters*, or *fixed oils* added as adulterants, will remain in the retort. These may be weighed in the retort, after heating it moderately and passing a current of coal-gas or air (previously filtered through cotton-wool) to separate any condensed steam and unvolatilised essential oils. The nature of the residue can then be ascertained by treating it with alcohol of 0.85 sp. gr. If wholly resinous it will dissolve, but fixed oils remain insoluble, with the exception of *castor oil*. To detect this, the alcoholic solution should be treated with an equal volume of sodium carbonate solution, and then boiled till the alcohol is driven off. Any *castor oil* will remain as an oily layer, but the *resin* will have dissolved in the alkaline liquid, and may be detected by separating any undissolved oil and acidulating with hydrochloric acid, when a turbid liquid will be formed from which resinous flocks or globules will gradually separate. In certain oils, however, a notable proportion of non-volatile stearoptene exists, such as in bergamot oil, which must not be confused with fixed matter added as an adulterant.

Oil of turpentine is readily detected when present in essential oils by a fractional distillation of the sample, and examination of the fraction distilling about 160°. Pinene, the characteristic constituent of oil of turpentine, may then be recognised by its b. p., and by the characters of its nitroso-chloride, etc. In cases where pinene is a normal constituent of the oil, the physical characters of the lightest fractions of the oil will frequently give the clue to its purity or otherwise.

The special methods for the detection of turpentine oil are given under the individual essential oils.

Another test for oil of turpentine and other adulterants of essential oils is founded on the solubility of the sample in alcohol, but as this is only a question of degree, and some of the more expensive oils closely simulate the behaviour of oil of turpentine itself, the inferences from the application of the test must be received with caution.   Essential oils differ considerably in their behaviour with alcohol, some undergoing solution much more readily than others.   These differences are, of course, dependent on the composition of the oils, and hence will not be strictly constant for different samples of oil of the same kind.

Instead of observing the number of volumes of alcohol of a certain strength which are required to effect solution of an essential oil Dowzard suggests that 5 c.c. of the oil should be mixed with 10 c.c. of alcohol of 0.799 sp. gr. at 15°, and water then added gradually from a burette until the liquid becomes turbid.   The end point is stated to be very distinct, although some of the more readily soluble oils show an opalescence before the liquid becomes distinctly turbid.   The volume of water in c.c. required to produce turbidity is multiplied by 100, and the product termed the "solubility value" of the oil.   Dowzard (*J. Soc. Chem. Ind.*, 1898, **17,** 1175) records the solubility values, sp. gr., and optical rotation of various oils.

The data on page 249 are tabulated from descriptions of essential oils given in the British Pharmacopœia (1898).   The figures are not in all cases justified by the facts.

PHARMACOPŒIAL CHARACTERS OF ESSENTIAL OILS (GREAT BRITAIN).

Oil	Sp. gr. at 15.5°	M. p., °	B. p., °	Optical rotation for 100 mm.	Other characters	Chief constituents
Anise	0.975 to 0.990 at 20°	10 to 15		-slight	Congeals at 10° to 15°	Anethole.
Cade	0.990				Sol. in ether, chloroform, partly in cold, but almost wholly in hot 90% alcohol.	Cadinene.
Cajuput	0.922 to 0.930				Bluish-green. Becomes semi-solid with phosphoric acid (sp. gr. 1.75).	Cineol.
Caraway	0.910 to 0.920				Almost colourless. Odour of the fruit, spicy taste.	Carvone.
Chamomile	0.905 to 0.915				Blue or greenish-blue when fresh.	Fatty esters.
Cinnamon	1.025 to 1.035				Pale green with ferric chloride, 50%¹ cinnamic aldehyde.	Cinnamic aldehyde.
Cloves	not below 1.050				Blue with ferric chloride. Becomes semi-solid (yellow) with strong ammonia.	Eugenol.
Copaiba	0.900 to 0.910			-28° to -35°¹	Sol. in 1 part absolute alcohol.	Caryophyllene.
Coriander	0.870 to 0.885				With 3 parts alcohol 70% gives clear solution.	Linalol.
Cubebs	0.910 to 0.930				Colourless, pale green or greenish-yellow.	Cadinene.
Dill	0.905 to 0.920			not less than +70°¹	Pale yellow, odour of the fruit, sweet taste.	Carvone.
Eucalyptus	0.910 to 0.930			not more than + or -10°	Semi-solid mass with phosphoric acid (1.75). Negative reaction with nitrite test.	Cineol.
Juniper	0.865 to 0.890				Sol. in 4 parts 95% alcohol.	Cadinene.
Lavender	not below 0.885				Sol. in 3 parts alcohol of 70%.	Linalyl acetate.
Lemon	0.857 to 0.860			not less than +59°¹	First 10% of distillate not different by more than 2°¹ in opt. rotation than original oil.	{ Limonene. Citral.
Mustard	1.018 to 1.030		147.2-152.2		First and last portions of distillate have same sp. gr. as original oil (absence of ethyl alcohol and petroleum).	Allyl thiocarbimide.
Nutmeg	0.870 to 0.910				Evaporated on water-bath leaves no crystalline residue (on cooling). (Absence of concrete oil of nutmeg.)	Myristicin.
Peppermint	0.900 to 0.920				Sol. in 4 parts alcohol of 70%. Cooled to -8.3° and menthol added gives considerable deposit.	Menthol.
Pimento	not less than 1.040				Semi-solid mass with equal vol. strong ammonia.	Eugenol.
Pine	0.865 to 0.870	19.4 to 22.2		-5° to -10°	Not more than 10% distils below 165°.	Sylvestrene.
Rose	0.856 to 0.860 at 30°				Pale yellow, crystalline, semi-solid oil.	Geraniol; citronellol.
Rosemary	0.900 to 0.915			not more than +10°	Sol. in 2 parts of alcohol of 90%.	Cineol; borneol.
Sandalwood	0.975 to 0.980			-16° to -20°³	Clear solution with 6 parts of alcohol of 70%.	Santal alcohols.
Spearmint	0.920 to 0.940				Sol. in equal volume of 95% alcohol.	Carvone.
Turpentine			160 to 180		Sol. in equal volume of glacial acetic acid.	Pinene.

¹ These figures or statements are not justified by the facts.

PHARMACOPŒIAL CHARACTERS OF ESSENTIAL OILS (UNITED STATES OF AMERICA).

Oil	Sp. gr. at 25°	Optical rotation for 100 mm.	Other characters	Chief constituents
Anise........	0.975 to 0.988	−2° at 25°	Congeals above 15°. Alcoholic solution neutral to litmus.	Anethole.
Cade........	....	....	Almost insoluble in water, but imparts to it an acid reaction, partially soluble in alcohol, completely soluble in ether.	Cadinene.
Cajuput........	0.915 to 0.925	not exceed −2° at 25°	Miscible with alcohol in all proportions. Alcoholic solution should be neutral.	Cineol.
Caraway........	0.900 to 0.910	Dextrogyrate +70° to +80° at 25°	Soluble in equal volume alcohol; colourless or pale yellow, thin liquid having a spicy taste.	Carvone.
Cinnamon........	1.045 to 1.055	1° + or −	Soluble in 2 volumes of 70% alcohol.	Cinnamic aldehyde.
Cloves........	1.040 to 1.060	....	Soluble in equal volume of alcohol, this solution being slightly acid to litmus.	Eugenol.
Copaiba........	0.895 to 0.905	Laevogyrate	Colourless or pale yellow liquid, slightly bitter and pungent taste.	Caryophyllene.
Corianler........	0.863 to 0.878	+7° to +14° at 25°	Soluble in 3 vols. 70% alcohol, and all proportions 80% to 90% alcohol.	
Cubeb........	0.905 to 0.925	−25° to −40°	Alcoholic solution is neutral to litmus. Soluble in all proportions of alcohol; colourless, pale yellow	Cineol.
Eucalyptus........	0.905 to 0.925	not more than +10° at 25°	colour, camphoraceous odour, and a pungent, spicy, and cooling taste.	
Juniper........	0.860 to 0.880	....	Colourless, faintly green or yellow liquid. Slightly bitter taste.	
Lavender........	0.875 to 0.910	....	Soluble in 3 parts 70% alcohol; colourless or yellow liquid, slightly bitter taste.	Linalyl acetate.
Lemon........	0.851 to 0.855	should not be less than +58°	Pale yellow liquid, somewhat bitter taste. First 10% of distillate should not differ more than 2° in rotation from that of original oil.	Citral.
Mustard (volatile)........	1.013 to 1.020	....	Miscible with alcohol in all proportions, forming clear solution. Both first and last portions of distillate should have same sp. gr. as original oil.	Allyl isothiocyanate.
Oil of myristica (nutmeg)	0.884 to 0.924	+	Soluble in equal volume alcohol, also soluble in 3 volumes of 90% alcohol; thin colourless or pale yellow liquid, having a warm, spicy taste.	
Peppermint........	0.894 to 0.914	−20° to −33°	Colourless liquid; strongly aromatic, pungent taste. Forms clear solution, neutral to litmus with an equal volume alcohol.	Menthol.

PHARMACOPŒIAL CHARACTERS OF ESSENTIAL OILS (UNITED STATES OF AMERICA) (CONTINUED).

Oil	Sp. gr. at 25°	Optical rotation for 100 mm.	Other characters	Chief constituents
Pimenta..............	1.028 to 1.048	......	Colourless, yellow, or reddish liquid; strong aromatic odour of allspice; a pungent, spicy taste. With 90% alcohol it is miscible in all proportions.	Eugenol.
Rose........	0.855 to 0.865	......	Pale yellowish, transparent liquid having strong fragrant odour of rose, and slightly sweetish taste. Congealing pt. should be between 18° and 22°.	Geraniol, citronellol.
Rosemary..............	0.894 to 0.912	+ not more than + 15°	The first 10% obtained by fractional distillation should also be +. Colourless or pale yellow, limpid liquid, and pungent odour of rosemary, somewhat camphoraceous taste. Soluble in about one-half volume or more of 90% alcohol.	Cineol, borneol.
Oil of santal (sandalwood)	0.965 to 0.980	not less than −16° nor more than −20°	Readily soluble in alcohol, solution being slightly acid to blue litmus. Pale yellow, somewhat thick liquid; a peculiar aromatic odour; pungent spicy taste.	Santal alcohols.
Spearmint.............	0.914 to 0.934	−35° to −48°	With an equal volume 86% alcohol forms a clear solution, which upon further dilution becomes turbid, a colourless, yellow, or greenish-yellow liquid, characteristic strong odour of spearmint and hot aromatic taste.	Carvone.
Turpentine.............	0.860 to 0.870	......	Soluble in 3 times its volume of alcohol. When distilled greater part should pass over between 155° and 162°. Thin colourless liquid having characteristic odour and taste, both of which become stronger and less pleasant by age and exposure to the air.	Pinene.

CONSTITUENTS OF ESSENTIAL OILS.

In the following table, the more abundant and commonly occurring constituents of natural essential oils are shown, but the list must not be regarded as exhaustive. There are a few constituents of certain essential oils, such as methyl alcohol, which do not fall naturally within any of the above-named classes, and the indefinite resinous substances produced by the oxidation of certain oils (*e. g.*, turpentine oil) are not included. On the other hand, certain substances—such as mentho-citronellol, ionone, piperonal, and nitrobenzene—though not constituents of natural essential oils, are closely related thereto, and have therefore been included in the table. No mention is made in the table of the remarkable colouring-matters present in certain essential oils.[1]

[1] The substance to which the blue colour of the oils of chamomile, wormwood, and mille-folium is due appears to be common to all blue essential oils, and is characterised by an absorption spectrum exhibiting 3 bands in the red and orange. It was called *cærulein* by W. H. Gladstone (*J. Chem. Soc.*, 1864). Piesse terms it *azulene*, and states that it boils at 281° to 289°. The name *trichamomillol* has also been suggested for it. Kachler (*Ber.*, 1871, p. 36) regards the colouring matter as a polymer of camphor of the formula $C_{30}H_{48}O_3$. By treatment with potassium it is reduced to a hydrocarbon boiling at 250° to 255°. Kremers has shown (Pharm. Review, 1901, **19**, 200) that the dark colour of the oil of wild bergamot is due to the presence of thymoquinhydrone, formed by the oxidation of thymoquinol.

TABLE OF PRINCIPAL CONSTITUENTS OF ESSENTIAL OILS.

Constituent	Formula	Sp. gr. at 15.5°	Optical rotation	B. p.	Refractive index at 20°	Chief Sources: Oil of:
Hydrocarbons.						
Paraffins	C_nH_{2n+2}					
Cymene	$C_{10}H_{14}$	0.860		175°	1.4846	*Pinus Sabiniana*, rose, etc. Wild thyme, cumin.
Terpenes, $C_{10}H_{16}$.						
Pinene		0.861	±40°	155°	1.4655	Turpentine.
Camphene		0.850 (at 50°)	±85°	160°	1.4621	Certain pine oils.
Limonene		0.848	+125°	177°	1.4746	Lemon, caraway.
Dipentene		0.848	0°	176°	1.4740	
Fenchene		0.864		156°	1.4690	Fennel.
Sylvestrene		0.851	+66°	178°	1.4747	Russian turpentine.
Carvestrine			0°	178°		Synthetic.
Phellandrene		(a) 0.846		170°	1.4732	Bitter fennel.
Phellandrene		(b) 0.848	+14.5°	170°	1.4759	Water fennel.
Terpinolene		0.855		190°		Isomerisation of other terpenes.
Terpinene		0.849	0°	180°	1.4846	Cardamons.
Thujene		0.851		151°	1.4760	
Sabinene		0.840		164°	1.4660	Savin.
Firpene		0.856	−47°	153°	1.4730	Certain fir oils.
Sesquiterpenes, $C_{15}H_{24}$.						
Cadinene		0.921	−98.6°	275°	1.5068	Oil of cade.
Caryophyllene		0.903	0°	259°	1.4998	Oil of cloves.
Clovene		0.932	0°	262°	1.5006	Artificial.
Cedrene		0.936	−80°	261°	1.5098	Cedar wood.
Humulene		0.900	−0.5°	263°		Hops.
Ledene				255°		Ledum palustre.
Patchoulene		0.945		255°		Patchouli.
Cannibene		0.897	−9°	258°		Cannabis indica.
Atractylene		0.913				Atractylis ovata.
Santalene (a)		0.9034	−14°	254°		Sandalwood.
Santalene (b)		0.9039	−28.5°	264°		Sandalwood.
Tingiberene		0.876	−7°	270°	1.4940	Ginger.

TABLE OF PRINCIPAL CONSTITUENTS OF ESSENTIAL OILS (CONTINUED).

Constituent	Formula	Sp. gr. at 15.5°	Optical rotation	B. p.	Refractive index at 20°	Chief sources: Oil of:
Olefinic Terpene-alcohols.						
Geraniol	$C_{10}H_{17}.OH$	0.880 to 0.883		230°	1.4780	Geranium, rose, palmarosa, etc.
Linalol	$C_{10}H_{17}.OH$	0.870 to 0.875	±20°	198°	1.4630	Linaloe, bergamot, lavender, etc.
Citronellol	$C_{10}H_{19}.OH$	0.858		225°	1.4570	Citronella, rose, geranium, etc.
Mentho-citronellol	$C_{10}H_{19}.OH$				1.4471	Artificially from menthone.
Nerol	$C_{10}H_{17}.OH$	0.8315 at 20°	+2°	95 to 105° at 7 mm., 225 to 227°	1.4776	Neroli, petitgrain.
Cyclic Terpene-alcohols.						
Borneol	$C_{10}H_{17}.OH$	0.861	±15°	212°		Borneo and Ngai camphor, oils of lavender, rosemary, etc.
Terpineol[1]	$C_{10}H_{17}.OH$					
Cineol[2] (Eucalyptol)	$C_{10}H_{18}O$	0.930	0°	176°		Eucalyptus, cajuput, wormseed.
Menthol	$C_{10}H_{19}.OH$	0.890	−50°	212 to 215°		Peppermint.
Sabinol	$C_{10}H_{15}.OH$	0.9432 at 20°		208 to 209°	1.4880	Savin.
Aromatic Alcohols.						
Benzyl alcohol	$C_6H_5.CH_2.OH$	1.0507		204.7°		Peru balsam, cherry laurel, jasmine, ylang-ylang.
Phenols and Phenolic Ethers.[3]						
Thymol	$C_{10}H_{13}.OH$	1.028		230°		Thyme, horsemint, ajowan, etc.
Carvacrol	$C_{10}H_{13}.OH$	0.981		236°		Origanum hirtum, satureja, etc.

[1] There are several isomers of the name terpineol, which are exceedingly difficult to isolate in a state of purity. For their relationships see Parry, Chemistry of Essential Oils, 2d edition, pp. 43–44.

[2] Cineol is not a true terpene-alcohol; it has apparently the constitution of a neutral oxide.

[3] Under this heading might be included para-cresol-methyl-ether, $C_6H_4.CH_3.OCH_3$, which occurs in ylang-ylang oil; guaiacol, $C_6H_4.OH.OCH_3$, the presence of which in birch-tar oil gives it the odour of Russia leather; and creosol, $C_6H_3.CH_3.OCH_3.OH$, also present in birch-tar oil. This oil and its constituents are, however, fully described in vol. 3.

TABLE OF PRINCIPAL CONSTITUENTS OF ESSENTIAL OILS (CONTINUED).

Constituent	Formula	Sp. gr. at 15.5°	Optical rotation	B. p.	Refractive index at 20°	Chief sources: Oil of:
Phenols and Phenolic Ethers. (*Continued*).						
Chavicol....	$C_9H_9.OH$	1.035 at 20°	0°	237°	....	Betel.
Methyl-chavicol....	$C_9H_9.OCH_3$	0.979 at 11.5°	....	215 to 210°	....	Sweet basil, bay, chervil.
Chavibetol....	$C_6H_3.(OCH_3).OH$	1.067 at 15°	....	254 to 255°	....	Dried betel.
Anethole....	$C_9H_9.OCH_3$	0.986 at 25°	....	232 to 234°	....	Anise and star-anise, fennel, etc.
Eugenol....	$C_6H_3.(OCH_3).OH$	1.072 at 14.5°	....	247°	1.5400	Clove, allspice, cinnamon-leaf, etc.
Methyl-eugenol....	$C_6H_3(OCH_3)_2$	1.041 at 11°	....	248 to 249°	....	Hazel-wort, citronella.
Safrole	$C_6H_3.O_2.CH_2$	1.108	....	232°	....	Sassafras, Japanese camphor, etc.
Apiole....	$C_6H_2.(OCH_3)_2.O_2.CH_2$	....	....	294°	....	Parsley-fruit.
Diosphenol (a palmitic ketone)..	$C_6H_4.OH.COH$	....	....	232°1	....	Buchu.
Asarole....	$C_3H_2.(OCH_3)_3$	1.165 at 18°	....	295 to 296°	....	Asarum, matico.
Aldehydes.						
Citral (Geranial)	$C_9H_{15}.COH$	0.897	0°	228 to 229°	1.4900	Lemon-grass, lemon, etc.
Citronellal	$C_9H_{17}.COH$	0.877	+.5°	205 to 210°	1.4480	Citronella, lemon, *Eucalyptus citriodora*, etc.
Benzoic aldehyde..	$C_6H_5.COH$	1.0504	....	179 to 180°	....	Bitter almonds, peach, cherry laurel, etc.
Cinnamic aldehyde..	$C_8H_7.COH$	1.0497 at 20°	....	130 at 30 m.m.	....	Cinnamon, cassia.
Salicylic aldehyde..	$C_6H_4.(OH).COH$	1.172	....	196.5°	....	*Spirza* oils, etc.
Anisic aldehyde..	$C_6H_4.(OCH_3).COH$	1.123	....	248°	....	Artificial hawthorn perfume.
Vanillin..	$C_6H_3(OH).(OCH_3).COH$	....	....	285°	....	Vanilla, gum benzoin, Peru balsam.
Piperonal (Heliotropin)	$C_6H_3.O_2.CH_2.COH$	....	....	263°	....	Artificial heliotrope perfume.
Cuminic aldehyde..	$C_6H_4.(C_3H_7).COH$	0.973	....	235°	....	Cumin, eucalyptus, etc.
Aromadendral..	$C_{10}H_{16}O$	0.947	....	210°	....	Certain eucalyptus oils.
Santalal..	$C_{15}H_{24}O$	0.9793	....	....	....	Sandalwood.

¹ Boils with decomposition.

TABLE OF PRINCIPAL CONSTITUENTS OF ESSENTIAL OILS (CONTINUED).

Constituent	Formula	Sp. gr. at 15.5°	Optical rotation	B. p.	Refractive index at 20°	Chief sources: Oil of:—
Ketones and Camphors.						
Methyl-amyl-ketone	$C_5H_{11}.CO.CH_3$	0.837 at 50°	....	151°	....	Cloves.
Methyl-nonyl-ketone	$C_9H_{19}.CO.CH_3$	0.8295 at 11°	....	224 to 225°	....	Rue.
Methyl-heptenone	$CH_3.CO(C_3H_5):(CH_3)C.CH$	0.853 at 20°	....	174°	1.4415	Lemon-grass, citronella, linalol.
Carvone	$C_{10}H_{14}O$	0.960 at 18°	+62°	224°	....	Caraway, fennel, dill, etc.
Fenchone	$C_{10}H_{16}O$	0.9465 at 19°	+72°	192 to 193°	1.4631	Fennel, thuja.
Thujone (tanacetone)[1]	$C_{10}H_{16}O$	0.9126 at 20°	−10°	201°	1.4503	Thuja, absinthe.
Pulegone	$C_{10}H_{16}O$	0.9333 at 20°	....	221 to 222°	....	Pennyroyal.
Laurel camphor	$C_{10}H_{16}O$	0.990	....	204°	....	Camphor, feverfew, etc.
Menthone	$C_{10}H_{18}O$	0.897	....	206°	....	American peppermint, etc.
Irone[2]	$C_{13}H_{20}O$	0.939 at 20°	....	144 at 16 mm.	....	Orris root.
Ionone[2]	$C_{13}H_{20}O$	0.9351	....	126 to 128° at 12 mm.	1.507	Artificial violet perfume.
Eudesmol	$C_{10}H_{18}O$	....	....	270 to 272°	....	Eucalyptus macrorhyncha, E. capitellata, E. camphora, etc.
Free Acids and Anhydrides.						
Benzoic acid	$C_6H_5.COOH$	....	....	249°	....	Ylang-ylang, also in gum benzoin, Tolu and Peru balsams.
Cinnamic acid	$C_8H_7.COOH$	1.247	....	300°	....	Liquid storax, Tolu and Peru balsams.
Salicylic acid	$C_6H_4(OH).COOH$	....	....	....	....	Wintergreen, birch, etc.
Coumaric acid	$C_6H_4(OH).(CH):COOH$	....	....	....	....	Melilotus officinalis, etc.
Coumaric anhydride (Coumarin)	$C_6H_4.O.(CH):CO$	....	....	290°	....	Tonka bean, woodruff, Melilotus, etc.
Esters.						
Methyl salicylate	$CH_3.C_7H_5O_2$	1.187	....	220 to 224°	....	Wintergreen, Betula lenta, etc.
Benzyl acetate	$C_6H_5.CH_2.C_2H_3O_2$	....	....	106°	....	Jasmine.

[1] These figures are for α-thujone. There is a less common form, β-thujone, present in oil of tansy.

[2] This is a mixture of 2 isomers (see Parry, Chemistry of Essential Oils, 2d edition, p. 486).

TABLE OF PRINCIPAL CONSTITUENTS OF ESSENTIAL OILS (CONTINUED).

Constituent	Formula	Sp. gr. at 15.5°	Optical rotation	B. p.	Refractive index at 20°	Chief sources: Oil of:—
Esters (*Continued*).						
Linalyl acetate	$C_{10}H_{17}.C_2H_3O_2$	0.912	±16°	105 at 11 mm.	......	Bergamot, lavender, jasmine.
Geranyl acetate	$C_{10}H_{17}.C_2H_3O_2$	0.9174	0°	242 to 245°	1.4628	Geranium.
Bornyl acetate	$C_{10}H_{17}.C_2H_3O_2$	0.991	−38°	98 at 10 mm.	1.4664	Pine-needles, thyme, golden rod, etc.
Bornyl valerate	$C_{10}H_{17}.C_5H_9O_2$	0.956	+20°	130 at 10 mm	1.4628	Valerian.
Menthyl acetate	$C_{10}H_{19}.C_2H_3O_2$	......	......	223°	......	Peppermint, etc.
Geranyl tiglate	$C_{10}H_{17}.C_5H_7O_2$					Geranium.
Methyl anthranilate	$C_6H_4(NH_2).CO.O.CH_3$	1.163 at 26°	......	132 at 14 mm	......	Neroli, jasmine, orange, lime flowers.
Sulphuretted Compounds.						
Dimethyl sulphide	$(CH_3)_2S$	......		101°		American peppermint.
Vinyl sulphide	$(C_2H_3)_2S$	0.9125				*Allium ursinum.*
Allyl Isothiocyanate (thiocarbimide).	$C_3H_5.NCS$	1.018		148°		Black mustard-seed, rape-seed.
Butyl (Secondary) Isothiocyanate.	$CH(CH_3).C_2H_5.NCS$	0.944 at 12°		160°		*Cochlearia officinalis.*
Acrinyl Isothiocyanate.	$C_3H_5O.NCS$	......				White mustard-seed.
Phenyl-ethyl Isothiocyanate	$C_2H_4(C_6H_5).NCS$	......				Mignonette-root.
Nitrogen Compounds.						
Hydrocyanic acid	HCN	0.697 at 18°		26.5°		Bitter almond, cherry-laurel.
Benzaldehyde-cyanhydrin	$C_6H_5.CH(OH).CN$					Bitter almond, cherry-laurel.
Trimethylamine	$N(CH_3)_3$	......		35°		Chenopodium.
Pyrrole	$C_4H_5.NH$	0.9752 at 12.5°		131°		Derivatives in orange oil from unripe fruit.
Indole	$C_6H_4(CH)_2:NH$	......	52°	245°¹		Jasmine.
β-Phenyl-propionitrile	$C_6H_5.C_2H_4.CN$			261°		Watercress (*Nasturtium officinale*).

¹ Boils with decomposition.
(For the characters of the sesquiterpene alcohols, see page 286.)

THE GERANIOL GROUP.

There exist in many essential oils several alcohols and their allied aldehydes, which are of the very highest value in perfumery, and which were, in the last edition of this work, described as olefinic terpene alcohols and aldehydes. This name appears to have little if anything to justify it, and as they are very few in number they may be better classified under the name of the principal member of the series, viz., geraniol.

They are open-chain compounds of intense and fine odour, and have the following physical characters:

	B. p.	Sp. gr.	Ref. index	Opt. rot.
Geraniol, $C_{10}H_{17}OH$......	229°	0.881	1.4780	Inactive.
Linalol, $C_{10}H_{17}OH$........	197°	0.872	1.4630	About ± 20°.
Nerol, $C_{10}H_{17}OH$.........	226°	0.881	1.4776	Inactive.
Citronellol, $C_{10}H_{19}OH$.....	118° (at 17 mm.)	0.855	1.4570	± 4° (approximate).
Citral, $C_{10}H_{16}O$..........	229°	0.897	1.4900	Inactive.
Citronellal, $C_{10}H_{18}O$.......	206°	0.877	1.4480	± 8° (approximate).

The above include all the substances of this group which can be regarded as definite chemical individuals. From time to time various other alcohols and aldehydes have been described as belonging to this series, but on careful examination none of them has been found to be other than a mixture of two or more of the above compounds. Such are coriandrol, from oil of coriander, which is merely impure linalol; nerolol from oil of neroli, which is identical with linalol; rhodinol, from rose oil, which appears to be a mixture of geraniol and citronellol; and so on.

Geraniol, $C_{10}H_{17}.OH.$

Geraniol is a monatomic primary open-chain alcohol, isomeric with linalol, which is a tertiary alcohol. The following formulæ probably express their constitution:

Geraniol. $(CH_3)_2C:CH.CH_2.CH_2.C(CH_3):CH.CH_2OH.$

Linalol. $(CH_3)_2C:CH.CH_2.CH_2.C(CH_3)OH.CH:CH_2.$
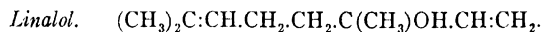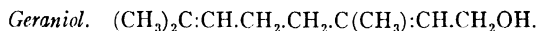
Geraniol is the principal constituent of true geranium oil, and of the oil of palmarosa, or so-called "Turkish geranium." It is also one

of the chief constituents of rose oil, and is present to a considerable extent in citronella oil and in smaller proportions in the oils of lavender, lemon-grass, and other oils.

Geraniol may be isolated from oils containing not less than 25% by converting it into its crystalline compound with calcium chloride, $(C_{10}H_{18}O)_2,CaC'_2.$ [1]

Geraniol may be prepared on a commercial scale (*German Patent*, No. 80007) by distilling geranium or pelargonium oil under reduced pressure (14 mm.), and heating the fraction which distils between 120° and 130° in an autoclave with acetic anhydride. The resulting esters are fractionated, distilled, the fraction passing over between 127° and 132° (consisting chiefly of geranyl acetate) saponified with alkali, and the liberated geraniol fractionated *in vacuo*. The portion distilling between 120° and 125° consists essentially of geraniol and forms the "rhodinol" of commerce.

As prepared by the foregoing methods, geraniol always contains more or less citronellol, from which it may be separated by converting it into acid geranyl phthalate in the manner prescribed by Flatau and Labbé (page 264).

Geraniol is a colourless oil, with a sweet rose-like odour, but lacking the fine odour of the oils in which it is an essential constituent. Its physical characters are given in the table on page 254. By careful oxidation with chromic acid it yields its aldehyde citral, and by heating with water in an autoclave to 200°, it is partly converted into its isomer linalol. Its esters are sweet-smelling liquids, and form important constituents of many essential oils. Geranyl acetate is a fragrant oil of sp. gr. 0.9174 and refractive index 1.4628. It boils at 129° at 16 mm. Geranyl tiglate forms the principal constituent (with free geraniol), of pelargonium leaf oil (true geranium oil).

Tiemann and Kruger recommend the following method for the purification of impure geraniol. It is treated with sodium, and the alcoholate is then treated with ether and phthalic anhydride, by which it is converted into geraniol-sodium-phthalate, which is hydrolysed by alkali hydroxide, and the pure geraniol precipitated by the addition of water.

[1] For the production of this substance, the oil, previously dried by anhydrous sodium sulphate, is intimately mixed in a mortar with an equal weight of recently fused calcium chloride. The mixture is kept under a desiccator for 24 hours, at or below 0°, and is then triturated with dry ether or petroleum ether. The liquid portion is separated by a suction filter and the crystalline mass treated with water, when the compound is decomposed and the liberated geraniol separates as an oily layer. This is separated and redistilled under reduced pressure.

Jacobsen detects geraniol in essential oils as follows:

The oil—or fractions boiling at 225° to 235°, so that at least 25% is present—is well mixed with an equal weight of dry powdered calcium chloride and the mixture kept in a desiccator at −4° for 12 to 16 hours. If the geraniol is present in the form of esters, it is of course saponified first.

The soft mass is rubbed with dry benzene, ether, or petroleum ether, and the liquid portion removed by a suction filter. The calcium chloride compound of geraniol is then treated with water, the oil separated, washed, and distilled under reduced pressure, when geraniol passes over at 230°.

Erdmann (*J. pr. Chem.*, 1897, [ii], **56,** 1) prefers to identify geraniol by treating it with diphenyl-carbamic chloride and pyridine on a water-bath. A current of steam removes diphenylamine and unaltered compounds, and the geraniol diphenyl-urethane is recrystallised from alcohol. It then melts at 82.2°.

Geraniol may be prepared from citral (geranaldehyde) by treating an alcoholic solution of that substance, feebly acidified with acetic acid, with sodium amalgam. To obtain a pure product, the solution should be heated with alkali to decompose unaltered citral, and steam-distilled, rejecting the last portions of the distillate.

On treatment with chromic acid mixture, geraniol is converted into *citral* or *geranial*, and on oxidation with permanganate it yields *iso-valeric acid*. Dehydrating agents convert geraniol into inactive *terpenes*.

By heating with acid anhydrides, geraniol is readily converted into the corresponding *esters*. Conversion into geranyl benzoate and acid phthalate is used for the purification of geraniol. Treatment with phthalic anhydride affords a sharp distinction between geraniol and linalol, the former being converted into an acid phthalate while the latter is not attacked (see under Linalol).

F. Tiemann (*Ber.*, 1898, **31, 2989**) states that when geraniol is heated with very strong alcoholic potassium hydroxide to 150° for eight hours, it is hydrolysed with formation of ethyl alcohol and *methyl-heptenol*, $(CMe_2:CH.CH_2.CH_2.CHMe.OH)$.[1] This compound boils at 85° to 86° under a pressure of 15 mm., and at 175° to 176° at the ordinary atmospheric pressure. Linalol remains almost unchanged when heated with strong alcoholic potassium hydroxide.

[1] According to P. Barbier, *dimethyl-heptenol* is the product of the reaction.

According to H. and E. Erdmann (*J. prakt. Chem.*, 1897, **56**, 1), if 1 drop of geraniol ("rhodinol") be diluted with 5 c.c. of alcohol, and 10 drops of strong sulphuric acid added without shaking, the acid sinks and takes an intense orange-yellow colour, while on gently moving the vessel the colour turns to reddish-violet at the surface of the junction of the two liquids. Linalol shows a similar reaction, but the colour is less stable and readily changes to brown. Citronellol gives a feebler colouration of a bluish tint.

Commercial Geraniol. Rhodinol.—Eckart orginally described the mixture of liquid alcohols from rose oil by the name of *rhodinol*, but it is now admitted, as pointed out above, that these and similar products consist essentially of geraniol with more or less citronellol, which, if not separated by special means, is always present in commercial geraniol.[1] The name rhodinol is now applied to the product from geranium oil and other sources.

By the action of dilute acids, many of the derivatives of geraniol are converted into cyclic isomerides of the same molecular weights, but having lower b. p., higher sp. gr., and somewhat lower indices of refraction than the open-chain compounds from which they are derived.

Linalol (Linalool), $C_{10}H_{17}.OH.$

Linalol is a monatomic open-chain alcohol, isomeric with geraniol (page 258), from which it differs in being optically active. Linalol is the essential constituent of oil of linaloe, and also exists, in the free state or in the form of esters, in the oils of petitgrain, bergamot, coriander, lavender, neroli, *Asarum Canadense*, etc.

Linalol exists in both the dextrorotatory and the lævorotatory forms. It is doubtful whether either form has been prepared in a state of absolute purity, so that the exact optical activity is unknown. Numerous specimens have been examined, but the figures generally represent a very impure product, but the following may be taken as the approximate values for the alcohol: Sp. gr. at 15°, o.868 to o.870; optical rotation, about +20°: refractive index at 20°, 1.4630, and b. p. 197° to 198° at ordinary pressure or 85° at 12 mm.

It is a colourless oil with a sweet odour, and forms an acetate which also exists in bergamot and lavender oil to a considerable extent. The

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[1] Varieties of geraniol also result from the practice of distilling the liquid over different flowers, to obtain products described as rose geraniol, mignonette-geraniol, etc., some of which are greatly preferable as perfumes to ordinary geraniol.

acetate is the typical odour-bearer in oil of bergamot, and that oil is rightly valued on its content of this ester. Linalyl acetate, $C_{10}H_{17}O$.-COCH$_3$, has a sp. gr. 0.912 and b. p. 105° to 108° at 12 mm. It can be prepared artificially by the action of acetic anhydride on linalol, and the artificial ester is an important commercial article, especially at times when bergamot oil is very scarce.   '

Linalol yields, among other products, some citral on oxidation.

Linalol is one of the alcohols that cannot be quantitatively determined by ecetylation, as decomposition takes place during the process (see under Estimation of Free Alcohols, p. 264).

Linalyl acetate is also a constituent of oil of petitgrain.

By treatment with hydrochloric acid, linalol yields a liquid *chloride* containing $C_{10}H_{18}Cl_2$, which has an odour like that of camphor, and by distillation with lime yields a *terpene* of characteristic odour boiling at 168° to 172°. Linalol combines with 4 atoms of bromine.

By treating linalol with acetic anhydride, and saponifying the linalyl acetate formed, Barbier obtained a product which he named licarhodol. K. Stephan (*J. pr. Chem.*, 1898, **58,** 109) states that a strongly dextro-rotatory, crystalline terpineol is formed under these conditions, and that Barbier's product was probably a mixture of this terpineol with linalol and geraniol. Stephan states that acetic acid does not act on linalol till the mixture is warmed, whereas concentrated formic acid readily converts lævo-linalol into dextro-terpineol, and dextro-linalol (coriandrol) into lævo-terpineol.

According to II. E. Burgess (*Analyst*, 1900, 265), linalol gives an immediate deep violet coloration when shaken with 2 or 3 times the quantity of a 10% solution of mercuric sulphate in 25% sulphuric acid.

Nerol.—This alcoholic substance was discovered in oil of neroli by Hesse and Zeitschel. The oil was freed as far as possible from geraniol by means of calcium chloride, and the phenylurethanes of the residuary alcohols were prepared. By fractional crystallisations, the nerol compound was obtained in a state of purity, and from it the alcohol was liberated in the usual manner.

Nerol is isomeric with geraniol and linalol, $C_{10}H_{17}OH$, and has a sp. gr. 0.8813, is optically inactive, and boils at 224° to 225° at ordinary pressure, and at 125° at 25 mm. Its diphenylurethane melts at 52° to 53°, which enables it to be sharply differentiated from geraniol. The relations between nerol and geraniol are

almost certainly stereoisomeric, their probable configurations being as follows:

$CH_3.C.CH_2.CH_2.CH:C(CH_3)_2$ $CH_3.C.CH_2.CH_2.CH:C(CH_3)_2$
$HC.:CH_2OH$ $CH_2(OH)C.H$
Nerol   Geraniol
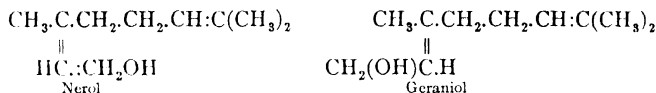
Their corresponding aldehydes are probably *a*-citral (geranial) and *b*-citral (neral). For these compounds see under Citral.

Citronellol, $C_{10}H_{19}.OH$.

Citronellol is an open-chain alcohol closely related to geraniol, from which it differs in formula by 2 atoms of hydrogen. It occurs in association with geraniol in rose oil, geranium oil, etc., and is also obtainable by the reduction of its aldehyde, citronellal,[1] which occurs in oil of citronella, etc.

Citronellol is a fragrant oily liquid, of 0.8565 sp. gr. at 17.5°, and a ref. index of 1.4570. It boils at 117° to 118°, under a pressure of 17 mm., and at the ordinary pressure, with some decomposition, at 225° to 230°.

Citronellol obtained by the reduction of citronellal exhibits a dextro-rotation of about $[a]_D = +4°$, whereas the variety isolated from rose oil is lævorotatory. In many specimens of geranium oil both varieties coexist. Both optical isomerides of citronellol yield *p*-methyl-adipic acid when oxidised with chromic acid mixture, and the product exhibits optical activity in the same sense as the alcohol from which it was derived.

Citronellyl acetate, $C_{10}H_{19}.C_2H_3O_2$, is a fragrant oily liquid, of 0.8928 sp. gr. at 17.5°. It boils at 120°, under a pressure of 15 mm. and exhibits dextrorotation ($[a]_D = +2.4°$).

The constitution of citronellol is, according to Tiemann and Schmidt, probably as follows:[2]

$$C(CH_3)_2:CH.CH_2.CH_2.CH(CH_3).CH_2.CH_2.OH.$$
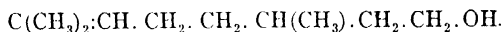
[1] Citronellol is not obtainable by direct action of nascent hydrogen on geraniol. If, however, a solution of geranic acid in boiling amylic alcohol be treated with sodium, citronellic acid is obtained, and when a mixture of calcium citronellate and formate is subjected to dry distillation citronellal is formed, which can be reduced to citronellol by treatment in alcoholic solution with sodium-amalgam. The compounds obtained by the foregoing processes are optically inactive.

[2] Barbier and Bouveault consider it to be: $CH_2: CMe. (CH_2)_3. CH Me. CH_2. CH_2. OH.$ and this formula seems preferable in view of the work of Harries and Schauwecker (*Ber.,* 1901, 34, 1498, 2981).

Citronellal, the aldehyde of citronellol (*q. v.*), is easily converted
into the closed-chain compound *iso*pulegol by heating with
acetic anhydride. Wallach has, conversely, succeeded in con-
verting the closed-chain compound menthone into an open-chain
alcohol isomeric with and much resembling citronellol. This he
terms mentho-citronellol. It is not certain whether it is a stere-
oïsomer of citronellol, or whether it is really identical with it. It has
a strong rose-like odour.

ESTIMATION OF OPEN-CHAIN ALCOHOLS IN ESSENTIAL OILS.

The estimation of the total alcohols present in essential oils may
be effected by converting them into their acetic esters (by treatment
with acetic anhydride) and ascertaining the amount of alkali required
for the saponification of the esters formed. The process, which is
described in detail on page 227, is vitiated by the presence of any
notable amount of citronellal, which is readily converted into isopu-
legyl acetate and thus renders the result too high. From oils contain-
ing them, the aldehydes should first be removed by treatment with
sodium hydrogen sulphite solution, the alcohols and other non-
aldehydic constituents extracted with ether, and the residue left on
evaporation of the ether employed for acetylation.

The accurate separation of the open-chain alcohols from each other
is attended with difficulty, and cannot in all cases be satisfactorily
performed. The separation of geraniol and citronellol may be ap-
proximately effected by the following method of Flatau and Labbé
(*Compt. rend.*, 1896, **122**, 1725): The oil is saponified with alcoholic
potassium hydroxide, and rectified *in vacuo*. The portion distilling
between 120° and 140° at 30 mm. pressure is dissolved, together with
an equal weight of phthalic anhydride, in an equal volume of pure
benzene. After boiling the mixture for an hour under a reflux con-
denser the benzene is evaporated off, and the residue treated with
sodium hydroxide. The gelatinous mass thus obtained is dissolved
in tepid water, and the solution shaken with ether to remove im-
purities. The esters are then liberated by adding hydrochloric acid
diluted with an equal volume of water, and washed out with petro-
leum ether at about 25°. The petroleum solution is then cooled to
—5°, when the *acid geranyl phthalate* separates out completely (in

the course of a week) in well-formed crystals.[1] On removing these
and evaporating the mother-liquor, the *acid citronellyl phthalate* is
left as a yellow oily residue which does not crystallise on cooling.
The two esters thus obtained are then saponified separately with 5%
alcoholic potassium hydroxide, and the liberated alcohols purified by
re-distillation in a current of steam.

By the above process, Flatau and Labbé obtained the following
percentages of open-chain alcohols from typical oils containing them:

Kind of oil	Total alcohols	Geraniol	Citronellol	Linalol
Indian geranium	80	63	17	. . . .
African (bourbon) geranium. . . .	80	10	70	. . . .
Melissa.	32	20	. . . .	12
Bulgarian rose	85 to 90	70	15	. . . .
Citronella.	46	40	6	. . . .

Schimmel & Co. state that the foregoing method is well suited
for the preparation of pure geraniol, since the crystals readily separate
and the alcohol obtained is as pure as that prepared by the calcium
chloride method.   On the other hand, the citronellol is always impure,
owing to geranyl phthalate being not wholly insoluble in petroleum
ether.   Hence the method is not suited for the quantitative estimation
of the two alcohols in essential oils.   To the inaccuracy of the method
Schimmel & Co. attribute the detection of 17% of citronellol in
palmarosa oil, a product which they assert contains mere traces,
if any, of that substance.

According to Tiemann and Schmidt (*Ber.*, 1896, **29,** 903), the
following method of detecting and estimating citronellol in admixture
with geraniol gives very satisfactory results:

A solution of 100 parts of the sample under examination in 100 parts
of absolute ether is cooled and added very gradually to a solution
(cooled to −10°) of 60 parts of phosphorus trichloride in 100 parts
of ether.   During this operation the temperature must not be allowed
to rise above 0°.   The mixture is allowed to stand for 4 or 5 days
at the ordinary temperature, and is then poured out on crushed ice,
the ethereal layer washed several times with ice-water and agitated

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[1] Geranyl phthalate crystallises in shining rhombic tablets which melt at 47°, and are
readily soluble in the usual solvents in the cold, and in petroleum spirit at 25°. It begins
to separate on cooling its solution in petroleum spirit to about 10°, and is almost insoluble
at −5°. Silver geranyl-phthalate is a white powder melting at 133.8° (?138.8). By
treating geranyl-phthalate dissolved in ether with bromine, a tetrabromo-derivative is
obtained melting at 114° to 115°. These compounds may be employed for the identifica-
tion of geraniol.

vigorously with dilute sodium hydroxide solution, which extracts from it citronellol (in the form of a chlorinated phosphorus ester acid), leaving behind geranyl chloride, etc. The alkaline solution is shaken once or twice with ether to remove impurities, rendered strongly alkaline, and steam-distilled in order to separate the liberated citronellol. The yield of citronellol is quantitative from samples containing not less than 20% of geraniol. Dextro-citronellol may be readily prepared in this way from citronella oil, which is first treated with sodium-amalgam in order to reduce the citronellal present, and the above process directly applied to the resulting mixture of alcohols.

The following figures are given by Tiemann and Schmidt as illustrating the application of the process to different oils:

	Total alcohols, %	Per 100 parts total alcohols	
		Geraniol	Citronellol
Turkish rose oil	80	75	(l—) 25
Spanish geranium oil	70	65	(l and d) 35
African geranium oil	75	80	(d and l) 20
Réunion geranium oil	80	50	(d and l) 50

The citronellol from réunion oil apparently contained traces of linalol. The so-called réuniol obtained by Hesse from the same source was found to be a mixture of geraniol with dextro- and lævo-citronellols, the latter modification predominating.

The method of acetylation, which is applicable to the estimation of the alcohol geraniol in a large number of oils, fails in the case of oil of citronella, since the isomeric body citronellal, present therein in considerable proportion, is by treatment with acetic anhydride converted quantitatively into the acetic ester of isopulegol. Hence the result will be a measure of the geraniol of the oil *plus* the citronellal present. Till recently, the figure so obtained was taken as the criterion of value of citronella oil, but Schimmel & Co. (*Report*, Oct., 1899) have proposed a method by which the actual geraniol present can be estimated, while the difference between the amount found and the result of the acetylation process gives the citronellal of the sample. Schimmel's method is based on the conversion of the geraniol into its acid phthalate by treatment with phthalic anhydride, which has no

action on citronellal. Secondary alcohols, like borneol, are scarcely attacked; while tertiary alcohols, such as linalol and terpineol, are wholly unaffected. Schimmel & Co. recommend that to 2 grm. of the oil under examination about 2 grm. of phthalic anhydride should be added, together with 2 c.c. of benzene, and the mixture heated on a water-bath for 2 hours in a flask furnished with a reflux condenser. After cooling, the mixture is shaken for 10 minutes with 60 c.c. (carefully measured) N/2 alkaline hydroxide solution, the flask being kept closed by a glass stopper. By this treatment the excess of phthalic anhydride is converted into potassium (or sodium) phthalate, and the acid geranyl phthalate into a neutral compound. The excess of alkali is then titrated back with N/2 sulphuric acid. The difference between the volume of standard acid required and that of the alkali originally employed is equivalent to the phthalic anhydride which has reacted with the geraniol. Thus 1 c.c. deficiency of normal alkali represents 0.148 grm. of phthalic anhydride ($C_8H_4O_3$), or 0.154 grm. of geraniol ($C_{10}H_{18}O$).

Citral, Geranial, $C_9H_{15}.COH$;

or, $(CH_3)_2C{:}CH.CH_2.CH_2.C(CH_3){:}CH.COH.$

This substance, also known as geranaldehyde, is usually spoken of as a definite compound, and for most practical purposes it may be so regarded. It is now clear, however, that 2 stereoisomeric forms of citral exist, both being present in lemon-grass oil which forms the principal source of commercial citral. (See under Nerol.)

Citral forms 70–85% of lemon-grass oil, and is present to the extent of about 4.5% in lemon oil. The oil of *Backhousia citriodora* also contains a large amount of citral, up to 95%.

Commercially, citral is of great importance, as it is the starting-point for the manufacture of ionone and allied compounds, which are the basis of the artificial violet perfumes so commonly used at the present time. Citral is a colourless or pale yellow liquid having a sp. gr. 0.890 or thereabouts. Commercial samples usually have a sp. gr. rather higher than this, due to the presence of a small quantity of impurities. It boils at 228°–230° at ordinary pressure, and at 110° at 12 mm. Its ref. index is about 1.4900, and it is optically inactive. The properties of the two isomers in a state of purity have been determined by Tiemann. The isomerism appears to be due to the

relative space positions of the $-CHO$ group and the H atom attached to a carbon atom in the molecule. This can be seen by an examination of the corresponding formulæ for geraniol and nerol (page 263), of which a-citral and b-citral are the aldehydes, respectively.

Tiemann's figures are as follows:

	a-Citral	b-Citral
Sp. gr.	0.8898	0.8880
B. p. at 20 mm.	118°	118°
Ref. index at 20°.	1.4891	1.4900

a-Citral yields a semicarbazone melting at 164°, while that of its isomer melts at 171°.

Citral forms a condensation product with cyanacetic acid, citralidene-cyanacetic acid, $C_9H_{15}.CH:C(CN)(COOH)$, m. p. 122°.

The methods of estimating citral are described on page 270, and are referred to under Lemon-grass and Lemon Oils.

Citral behaves similarly to citronellal (*vide infra*) when treated with molecular proportions of pyroracemic acid and β-naphthylamine. The citral-β-naphthocinchoninic acid obtained forms lemon-yellow laminæ, m. p. 197°.

F. Tiemann has pointed out (*Ber.*, 1898, **31,** 3324) that if the citral is not present in theoretical proportion, the pyruvic or pyroracemic acid is partially decomposed, and α-methyl-β-cinchoninic acid is formed, melting at 210°. In addition, a neutral substance is produced, which can only be separated by repeatedly dissolving the acid in ammonia, and reprecipitating it by acetic acid. Pure citral gives about 45% of the theoretical yield (or nearly its own weight) of citryl-β-naphtho-cinchoninic acid. If Doebner's reaction be applied to a mixture of citral and citronellal, the citryl compound crystallises out first, and citronellyl-β-naphtho-cinchoninic acid, melting at 225°, can be obtained from the mother-liquor. Tiemann states that 10% of citronellal in citral can be detected with certainty in this manner.

By treatment with hydriodic acid or potassium hydrogen sulphate citral is converted quantitatively into *cymene*, $C_{10}H_{14}$. This reaction confirms the constitutional formula already given.

When treated with silver oxide and ammonia, citral is converted into the corresponding acid, *geranic acid*, $C_{10}H_{16}O_2$.

Citronellal, Citronellic Aldehyde, $C_9H_{17}.COH$.

Citronellal occurs in large proportion (30 to 50%) in oil of citronella, and in certain kinds of geranium oil. It is also present in the oil of *Eucalyptus maculata* (var. *citriodora*).

Citronellal is a colourless oily liquid, of agreeable citronella-like odour. It is optically active ($[a]_D$ = about $\pm 8°$),[1] has a sp. gr. of 0.8768 at 17.5°, and a ref. index of 1.4481. It boils and distils with slight decomposition between 205° and 208°. E. J. Parry found the purest commercial substance to have a sp. gr. of 0.873 and to be only slightly optically active.

By the action of reducing agents (sodium amalgam), citronellal is converted into the corresponding alcohol, *citronellol*, $C_{10}H_{19}.OH$.

When heated with acetic anhydride, citronellal is converted into the isomeric cyclic alcohol, *isopulegol*,[2] closely resembling pulegol. This and other reactions support the following constitutional formula for citronellal:

$C(CH_3)_2:CH.CH_2.CH_2.CH(CH_3).CH_2.COH.$ The formula
$CH_2:C(CH_3).CH_2.CH_2.CH_2.CH(CH_3).CH_2.COH$
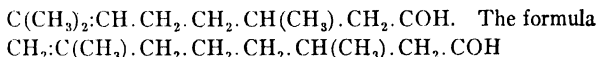
is preferred by Harries and Schauwecker (*Ber.*, 1901, **34,** 2981).

Labbé states (*Ber.*, 1899, **32,** 3338) that pure citronellal is apt to undergo complete and rapid isomeric change into *isopulegol*.

Citronellal was formerly regarded as a ketone, and hence was designated *citronellone*, but its aldehydic constitution appears to be established by a reaction observed by O. Doebner (*Ber.*, 1894, **27,** 352), which depends on the formation of *citronellyl-β-naphthocinchoninic acid*. This compound is prepared by treating citronellal (more than 1 molecule), dissolved in absolute alcohol, with a solution of 1 molecule of pyroracemic (pyruvic) acid in the same menstruum, and adding a solution of 1 molecule of β-naphthylamine in absolute alcohol. The mixture is heated on a water-bath for 3 hours and then allowed to cool, when the acid crystallises out in colourless needles melting at 225°. Doebner recommends the reaction for the detection and estimation of citronellal in essential oils.

[1] According to Tiemann and Schmidt (*Ber.*, 1896, **29,** 903), citronellal exists in 2 optically opposed modifications, which on oxidation with chromic acid mixture yield the corresponding dextro- and lævo-*β-methyladipic acids*, $(CO.OH)CH_2.CH_2.CH(CH_3).CH_2.-CO.OH$. Acetone is simultaneously formed.

[2] Commercial citronellal is a colourless, slightly dextrorotatory liquid of about 0.873 sp. gr. On treatment with sodium hydrogen sulphite and carbon dioxide, it leaves about 6% of residue smelling of isopulegol (peppermint-like odour) and containing alcohols (probably geraniol and citronellol in small quantity. On oxidation with chromic acid mixture, this residue yields *isopulegone* (F. Tiemann, *Ber.*, 1899, p. 825).

Citronellal reacts violently with free sulphurous acid, terpenes and other products being formed, and a similar action takes place with sodium hydrogen sulphite containing free acid. The compound, $C_9H_{17}.COH,NaHSO_3$, is best prepared by treating the aldehyde with an ice-cold solution of neutral sodium sulphite to which the calculated quantity of acetic acid has been added.◆ So prepared, and purified by kneading with alcohol and washing with ether, the compound is quite stable. It is quantitatively decomposed by sodium hydroxide or carbonate at the ordinary temperature. By the action of bisulphite solution, containing sulphite, on citronellal or its bisulphite compound, a compound is formed having the formula C_9H_{18}-$(SO_3Na).CH(OH).SO_3Na$. By the action of sodium carbonate this is converted into the *hydrosulphonate*, $C_9H_{18}(SO_3Na).CHO$, from which sodium hydroxide does not liberate citronellal, even on boiling.

On treatment with hydroxylamine, citronellal yields an *oxime*, $C_{10}H_{18}NOH$, as an oil of o.906 sp. gr., b. p. 135° at 14 mm. pressure.

H. E. Burgess has observed (*Analyst*, 1900, page 265) that citronellal gives a bright yellow colour, which is fairly permanent, when a little of the aldehyde is shaken with 2 or 3 times the quantity of a 10% solution of mercuric sulphate in diluted sulphuric acid (25%). Citral gives a bright red evanescent coloration.

Estimation of Citral and Citronellal.

The estimation of citral in essential oils is attended with peculiar difficulties.[1] Theoretically it should be possible to reduce the aldehyde to geraniol, which could then be acetylated and saponified, and a process on these lines has been described by H. Garnett (*Pharm. J.*, **56,** 321), but the alteration cannot be relied on to take place quantitatively. Every change is accompanied by the formation of by-products of resinification, such as methyl-heptenone, acetone, cymene, etc. This is the case even when the reduction of the citral to geraniol is conducted in alcoholic solution. The usual process based on the production of the acid sulphite compound of citral is also open to exception, owing to the unavoidable formation of soluble sulphonic compounds.[2] Hence the method may be useful for ascertaining the

[1] Except in cases such as that of lemon-grass oil, which contains a large proportion of this aldehyde.
[2] In the process of Tiemann, described on page 272, advantage is taken of this tendency and an apparently accurate method based thereon.

comparative value of commercial samples of oils containing citral
but not for the accurate estimation of the proportion of aldehydes
unless they are present in large amount.

The condensation product of citral with cyanacetic acid has been
described by F. Tiemann (*Ber.*, 1898, **31,** 3329) as a readily crystal-
lisable compound, well adapted for the detection and estimation of
citral in essential oils. A solution of cyanacetic acid in 3 parts
of water is mixed with 2 equivalent proportions of sodium hydroxide
(in the form of a 30% solution), and 1 equivalent proportion of
citral then shaken with the alkaline liquid. Pure citral dissolves
completely, and on acidifying the liquid, the citralidene-cyanacetic
acid separates as an oil which soon becomes crystalline. The product,
which is from 92 to 95% of the theoretical, is recrystallised from
warm benzene or from a mixture of benzene and petroleum spirit,
when a yield of 73 to 75% of the theoretical is obtained, the resulting
yellow crystals melting at 122°, and having the composition C_9H_{15}.-
CH:C(CN)COOH. The citral in essential oils may be estimated
by shaking the oil with an alkaline solution of the cyanacetic acid.
After repeatedly shaking out the alkaline liquid with ether, the citral
compound is liberated by acidifying the liquid.

E. J. Parry first concentrates the oil to be examined for citral
(lemon oil) by distilling off about 85% of the terpene at a pressure of
12 to 13 mm. The distillate contains only the merest traces of
citral. 200 c.c. of the oil thus yields about 25 c.c. of concentrated
residue, the sp. gr. of which is first determined. 10 c.c. of the liquid
is then shaken with a solution of about 5 grm. of cyanacetic acid and
an equal weight of sodium hydroxide in 30 c.c. of water, the operation
being performed in a small absorption flask having a long, graduated
neck. The unabsorbed portion of the oil is measured,[1] and the per-
centage of citral thus obtained, after correcting for the sp. gr. of citral
(0.897). The sp. gr. of citral is so near to that of the concentrated oil
that they may be taken as identical. Parry states that the method has
given fairly accurate results in his hands and the value of the method
has been confirmed by Schimmel & Co. The cyanacetic acid must,
however, be *quite* fresh, as there is reason to believe that it changes on
keeping and then gives erratic results.

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[1] A little trouble in measurement sometimes occurs, owing to the stearoptene of the oil
forming a layer on the surface of the liquid, but in Parry's opinion the difficulty is trifling.
It may be wholly overcome by steam-distilling the citral from the concentrated residue,
and operating on the steam distillate.

F. Tiemann (*Ber.*, 1898, **31,** 3297) has shown that the reaction of citral with alkali-metal sulphites varies with the conditions of the experiment. Thus on agitating 100 parts of citral with 100 of sodium hydrogen sulphite dissolved in 200 parts of water and 25 parts of glacial acetic acid, the normal bisulphite compound, $C_9H_{15}.CHO$, $NaHSO_3$, is formed quantitatively. Partial dissociation occurs on dissolving the compound in warm water, and on regenerating the citral a loss of from 10 to 15% always occurs from a partial conversion of the normal compound into a hydrosulphonic acid derivative. A stable dihydrosulphonate, $C_9H_{17}(SO_3Na)_2.CHO$, not decomposed by alkali-metal carbonates or hydroxides, is obtained by the action of excess of bisulphite solution (which must be maintained acid throughout) on the hydrogen sulphite compound. An unstable dihydrosulphonate of the same formula as the above is obtained by the action of a slightly alkaline solution of sodium sulphite on citral or its normal bisulphite compound. For its formation, Tiemann recommends that 100 parts of citral should be shaken with 350 parts of sodium sulphite, Na_2SO_3, 7aq, and 125 parts of sodium bicarbonate for several hours. The product is then extracted with ether to remove non-aldehydic impurities, and the citral liberated by sodium hydroxide. The solution of alkali should be previously saturated with ether, a layer of ether poured on the aqueous solution, and the sodium hydroxide added gradually, so as to expose the citral to its action for as short a time as possible. Tiemann recommends this process for the estimation of citral in lemon-grass oil. Under the prescribed conditions, geraniol and linalol do not form hydrosulphonates, while citronellal is converted into sodium citronellylhydrosulphonate, which is not decomposed by sodium hydroxide, even on boiling.

Tiemann gives the following results of estimation of citral in sample of lemon-grass oil by 3 methods:

	Cyanacetic acid method, %	NaHSO₃ method, %	Na₂SO₃ and NaHCO₃ method, %
Non-aldehydic constituents	18, free from citral	24 citral present	20, containing a little citral.
Citral, by difference. .	82	76	80
Citral, by direct determination.	75.4	65	77.5
Citral, loss in direct determination.	6.6	11	2.5

The cyanacetic acid method is to be preferred for the estimation of the non-aldehydic constituents, and the alkaline sulphite method for the estimation of the actual citral.

F. Tiemann states that the last method has the advantage that citronellal does not affect the estimation of the citral, but he denies the statement of Flatau a.nd Labbé that a notable proportion (6 to 8%) of citronellal is present in lemon-grass oil.[1] Tiemann (Ber., 1899, **32,** 812) also points out certain differences in the behaviour of citral and citronellal with sulphites which may be utilised for their separation. Thus citronellal is not attacked by a 10% solution of sodium sulphite $(Na_2SO_3. 7H_2O)$ in presence of sodium bicarbonate, and hence may be extracted together with the non-aldehydic substances by ether, whereas citral is completely converted under the same conditions into the unstable dihydrosulphonate already described. On the other hand, if a mixture of the aldehydes be shaken with excess of *concentrated* sodium sulphite and bicarbonate solutions, citronellal is converted into the normal bisulphite compound, which separates, and citral into the unstable dihydrosulphonate. If in this process the theoretical quantity or only a slight excess of sulphite be used, the citral compound is formed by preference, and the citronellal can be extracted unchanged by ether. By applying the process to lemon-grass oil, and shaking the residue freed from citral with a concentrated solution of sodium sulphite and bicarbonate, Tiemann obtained o. 2 grm. of the citronellal bisulphite compound from 300 grm. of oil. If a mixture of the aldehydes be shaken with sodium sulphite solution while a current of carbon dioxide is passed through it, the citral is converted into the unstable dihydrosulphonate, while the citronellal forms the hydrosulphonate, which is not decomposed by sodium hydroxide. If methyl-heptenone be also present (as in lemon-grass oil), the citral may he extracted by a 10% solution of sodium sulphite containing bicarbonate, the citronellal by a concentrated solution of the same kind, and finally the methyl-heptenone by an ice-cold solution of sodium bisulphite in 1.5 parts of water.

Doebner recommends the following process for the separation of citral and citronellal. The mixture of aldehydes is digested with

[1] According to Flatau and Labbé (Bull. Soc. Chim., 1898, **19,** 1012; 1899, **21,** 77), if the normal bisulphite compounds of citral and citronellal are treated with a solution of barium chloride, citryl sulphite remains in solution while the citronellal is precipitated quantitatively as $Ba(SO_3,C_{10}H_{19}O)_2$, but Tiemann (Ber., 1899, **22,** 812) states that the normal bisulphite compound of citral gives a copious precipitate with barium chloride, though the precipitation is not complete; while the precipitation of the normal citronellal compound is not perfect.

pyruvic acid and β-naphthylamine, when condensation products of the aldehydes and β-naphthocinchoninic acid are formed. The citral compound is less soluble than the citronellal compound and can easily be crystallised out first. The citral compound melts at 197°, while the citronellal compound melts at 215°.

Burgess and Child (see also under Aldehydes, p. 233) have adopted the following modifications of the bisulphite method and of the sulphite method of F. Tiemann for the estimation of the aldehydes (citral, etc.) in lemon oil. Both methods are stated to yield almost theoretical results when the following details are adhered to carefully:

1. In the estimation of the aldehydes by the sodium hydrogen sulphite method, a 40% solution of the reagent is most convenient, and a strongly acid solution should be avoided. 25 c.c. of lemon oil is mixed with 75 c.c. of 40% sodium metabisulphite solution and 25 c.c. of sodium sulphite (made by exactly neutralising sodium hydrogen sulphite solution with a 10% solution of sodium hydroxide) in a suitable flask. (See *Analyst*, 1900, 197.) The temperature is then raised to about 70° and the solution thoroughly shaken for 1 hour. The addition of sodium sulphite is indispensable, owing to the fact that it forms a soluble sulphonic compound and a clear meniscus is thus obtained. The oil is then raised into the measuring burette, and the diminution in volume gives the amount of total aldehydes.[1] A correction must be made for the solubility of the terpenes in solution. Burgess and Child subtract 0.35 c.c. from the reading, but it is advisable for each worker to determine this correction.

2. The following method depends upon the fact, discovered by F. Tiemann, that if citral be agitated with a neutral solution of sodium sulphite, a soluble sodium sulphonic acid salt is produced. Burgess and Child have taken advantage of the formation of sodium hydroxide in the reaction to make an addition

$$C_9H_{15}.CHO + 2Na_2SO_3 + 2H_2O = C_9H_{17}.(NaSO_3)_2.COH + 2NaOH.$$
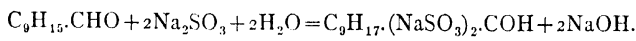
of phenolphthaleïn to the solution, to indicate the point when all the citral has combined to form the soluble compound. For the estimation a saturated solution of sodium sulphite is prepared, and, if acid, is neutralised with a solution of sodium hydroxide until a faint pink

[1] This method may also be used for solutions containing high percentages of citral, using from 5 to 20 c.c. of the solution and measuring in a Hirschsohn or similar flask.

colour is permanently maintained with phenolphthaleïn. To 50 c.c. of this solution 25 c.c. of the oil is added, and 2 drops of an alcoholic solution of phenolphthaleïn. The whole is then heated on the water-bath nearly to b. p., with constant shaking. A deep red colour almost at once appears, showing that the action has commenced. A few drops of sulphurous acid are then cautiously added, and the heating continued until no further colour is produced after a further addition of the sulphurous acid. The oil is then measured as described above. The obvious advantage of this method is that the end of the reaction may be ascertained to a certainty, while the bisulphite process depends on the continual shaking for a period of not less than 1 hour.

Assay Method of the United States Pharmacopœia.

This method is that of Sadtler (see *J. Soc. Chem. Ind.*, 1905, **24**, 1193).

Introduce into a counterpoised 150 c.c. flask, by means of a pipette, about 15 c.c. of oil of lemon, and note the exact weight; add 5 c.c. of distilled water and a few drops of rosolic acid test solution, and then neutralise the liquid exactly by the cautious addition of N/10 sodium hydroxide. Add 25 c.c. of a neutral solution of sodium sulphite (1 in 5) and immerse the flask in a water-bath containing boiling water. From a burette add, as needed, just sufficient N/2 hydrochloric acid to maintain the neutrality of the mixture, keeping the flask continuously heated and frequently agitated, and adding a drop or two of rosolic acid. When a permanent condition of neutrality is reached, note the number of c.c. of the N/2 hydrochloric acid consumed. Carry out a blank test, identical with the foregoing, except that the oil of lemon is omitted, and note the amount of N/2 hydrochloric acid consumed. Subtract the number of c.c. required in the blank test from the number required in the original test; each c.c. of this difference corresponds to 0.03802 grm. of citral. To find the percentage, multiply the above difference by 0.03802, and this product by 100, and divide by the weight of the oil of lemon taken.

Other processes for the estimation of citral in essential oils have been suggested, namely, the formation of the oxime with hydroxylamine in alcoholic solution and subsequent titration of the excess of hydroxylamine with hydrochloric acid; and the cyanacetic acid process of Tiemann already described (page 233).

The chief fault of the hydroxylamine process is that the end-point
is not as well defined as could be desired. The most useful process
is that described by Walther (*Pharm. Cent.*, 1899, **40,** 621), slightly
modified by Bennett (*Analyst*, **34,** 394, 14).

The process is carried out as follows:

20 c.c. of a solution of hydroxylamine hydrochloride in 80% alcohol
(half-normal strength), are exactly neutralised to phenolphthaleïn
with a solution of sodium hydroxide in alcohol, and added to 20 c.c.
of lemon oil (for example) and 20 c.c. of alcohol. The mixture is
boiled gently under a reflux condenser for half an hour and allowed to
cool. The condenser is washed down, and the contents of the flask
diluted to 200 c.c. with water, and neutralised to phenolphthaleïn.
The liquid is then titrated with $N/2$ sulphuric acid using methyl-
orange as indicator. A blank experiment is carried out at the same
time, and the necessary deduction made. Each c.c. of acid used for
the neutralisation represents an equivalent amount of hydroxylamine
that has combined with the citral, and is equivalent to 0.076 gr. of
citral. Bennett prefers to determine the end-point by spotting on a
white plate. He states that the end-point is sharper in this way.

Walther originally proposed to use sodium hydrogen carbonate to
neutralise the hydrochloric acid of the hydroxylamine salt, but it is
probable that the liberated CO_2 carries off a little hydroxylamine.

Burgess and Child obtained the following results by the foregoing
methods (*J. Soc. Chem. Ind.*, 1901, **20,** 1179):

Nominal % of citral in lemon terpenes	Sodium bi- and mono- sulphite I	Sodium sulphite II	Hydroxyl- amine III	Cyanacetic acid IV
2.5	2.2 (2.1)[1]	2.2 (2.1)[1]	2.6 (2.4)[1]	
5.0	4.4 (4.2)	4.0 (4.2)	5.0 (4.8)	
7.5	6.5 (6.3)	6.4 (6.3)	7.1 (7.2)	
10.0	8.6 (8.6)	8.4 (8.6)	9.6 (9.6)	
Commercial citral	84 %	84 %		100%
Terpeneless lemon oil	46.5%	45.5%	46.6%	62%[2]
Lemon-grass oil	75 %	75 %		97%

[1] The figures in parentheses show the calculated citral present.
[2] See E. J. Parry (*J. Soc. Chem. Ind.*, 1901, **20,** 1182).

CYCLIC TERPENE ALCOHOLS.

The substances of this class occurring naturally in essential oils are tabulated on page 254.

Bo:neol, Bornyl Alcohol, $C_{10}H_{17}OH$.

Borneol is one of the series of naturally occurring alcohols belonging to what is conveniently described as the "camphor series." These alcohols have, in most cases, corresponding ketones which occur naturally, so that they are mostly secondary alcohols. The following are the principal members of the series:

Alcohol	*Ketone*
Borneol.	Camphor.
*Iso*borneol.	
Fenchyl alcohol.	Fenchone.
Thujyl alcohol.	Thujone.
Terpineol.	
Pulegol.	Pulegone.
Menthol.	Menthone.

Borneol occurs as dextro-borneol in the wood of *Dryobalanops camphora* (Borneo camphor) and as lævo-borneol in *Blumea balsamifera* (Ngai camphor). It probably occurs also in the optically inactive variety, and in the essential oil of Virginian snake-root (*Aristolochia serpentaria*).

Borneol forms the main constituent of "*Borneo camphor.*" This, as imported, contains from 2 to 3.5% of resin and other impurities, from which the borneol can be separated by sublimation. Borneol may also be obtained by the action of sodium or of alcoholic potassium hydroxide on common camphor.

Borneol forms regular crystals which are lighter than water. It has an odour like that of camphor and a pungent peppery taste. Borneol melts at 203° and boils at 212°; but it sublimes readily below its m. p. and condenses in hexagonal plates.

Borneol is very sparingly soluble in water, but soluble in alcohol, ether, and petroleum spirit.

Natural dextro-borneol has a specific rotation of $[a]_D = +33°$, while that of the artificial product is $+43°$. But natural *lævorotatory*

borneol occurs nearly pure in *Ngai camphor*, and less pure in *Bang Phien*. It is also present in the oils of lavender, rosemary, spike, etc. The fusel oil of the spirit obtained by the fermentation of the sugar of madder contains *l*-borneol, which is said by Haller also to occur in the forms of acetate, formate, and valerate in the oil of valerian.

According to Haller, a racemoid modification of borneol, consisting of a mixture of dextro- and lævo-borneols in equal proportions, is obtained by the distillation of the crude "terebene" resulting from the action of sulphuric acid on turpentine oil.

An optically inactive borneol, m. p. 199°, was obtained from colophony by Armstrong and Fielden.

Borneol forms a series of esters of which several are to be found in various essential oils. The following are the characters of the principal of these esters:

	B. p.	Sp. rot.	Sp. gr.	Ref. index at 15°
Formate	90°	+31°	1.013	1.47078
Acetate	98°	−38° 20′	0.991	1.46635
Propionate	110°	+24°	0.978	1.46435
Butyrate	121°	+22°	0.966	1.46380
Valerate	128–130°	+20°	0.956	1.46280

Borneol forms a phenylurethane, m. p. 138°. It also forms crystalline compounds with chloral and bromal, the former melting at 55°, and the latter at 98°.

Bredt considers that borneol is stereoisomeric with *isoborneol* (*q. v.*), the OH group being turned away from the ring in borneol, and toward the centre in *iso*borneol. He thus terms borneol *exo*borneol, and *iso*borneol *endo*borneol.

Isoborneol.—The borneol obtained by the reduction of camphor is stated to contain an admixture of a modification known as *isoborneol*, which is also obtained by warming camphene with acetic acid and a little sulphuric acid, and decomposing the acetate formed by alcoholic potassium hydroxide. This reaction is employed by Bertram and Walbaum (*J. pr. Chem.*, 1894, [2], **49,** 15) for the detection of camphene in the oils of lemon, ginger, etc.

*Iso*borneol agrees with the ordinary modification in yielding camphor, etc., on oxidation by dilute nitric acid, but according to Bertram and Walbaum exhibits the following differences:

	Borneol	Isoborneol
Crystalline form..	Hexagonal	Hexagonal laminæ.
M. p.....	203	212
B. p........	212	....
Solubility in benzene, at 0°......................	1 : 7	1 : 3
Solubility in petroleum ether at 0°...................	1 : 10	1 : 4
M. p. of chloral com, ound........	55 to 56	liquid
M. p. of bromal compound....	98 to 99	71 to 72
Acetate.....	29	liquid
Acetate; b. p. at 15 mm. pressure, °.................	106 to 107	107
Sp. rot....	43°	.4

Dehydrating agents convert isoborneol into *camphene*, whereas borneol is unaffected. *Iso*borneol is converted into the corresponding ether when boiled with sulphuric acid and methyl or ethyl alcohol, whereas borneol does not yield ethers by this treatment.[1]

L. A. Tschougaef (*Bull. Soc. Chem.*, 1901, **26**, 298); purifies borneol from *iso*borneol by converting the alcoholate of borneol into methyl bornyl-xanthate, when steam-distillation removes the *iso*borneol. When heated with alcoholic potassium hydroxide and the liquid acidified the methyl ester yields borneol. According to Bredt, the formulæ for borneol and its ketone, camphor, are as follow:

Borneol

$$CH_2—CH—CH_2$$
$$| \quad | \quad |$$
$$| \quad CMe_2 \quad |$$
$$| \quad | \quad |$$
$$CH_2—CMe—CH.OH$$

Camphor

$$CH_2—CH—CH_2$$
$$| \quad | \quad |$$
$$| \quad CMe_2 \quad |$$
$$| \quad | \quad |$$
$$CH_2 — CMe—CO$$
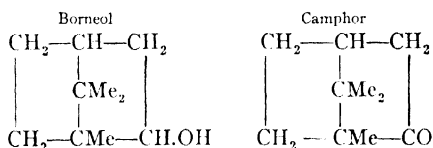
Fenchyl Alcohol, $C_{10}H_{17}OH$.

Fenchyl alcohol does not probably occur naturally, but is here mentioned on account of its connection with fenchone, its ketone, which is to be found in oil of fennel and oil of thuja. It is prepared by the reduction of the ketone, and forms a crystalline mass, m. p. 45°, b. p. 200°. Its sp. gr. is 0.933 at 50°. It is obtained in both optically active varieties, that from dextro-fenchone being lævorotatory, while that from lævorotatory fenchone is dextrorotatory. The sp. rot. is about 10°. The terpene fenchone can be hydrated by treatment with sulphuric and acetic acids, and on hydrolysis of the resulting ester

[1] According to F. W. Semmler (*Ber.*, 1900, **33**, 774), isoborneol on being heated with zinc-dust at 220° yields, as the chief product, *isodihydro-camphene*, $C_{10}H_{18}$, melting at 85°; whereas borneol remains unchanged when similarly treated. Since zinc is capable of removing oxygen from tertiary alcohols only (abst. *J. C. S.*, 1894, **1**, 611), the view that borneol and *iso*borneol are physical isomerides is untenable, the former being a secondary and the latter a tertiary alcohol.

*iso*fenchyl alcohol is obtained, m. p. 62°. This body is related to fenchyl alcohol in the same way as *iso*borneol to borneol.

Thujyl Alcohol, $C_{10}H_{17}OH$.

This substance has not been found naturally, but is mentioned for the same reason as fenchyl alcohol. It is the alcohol of the ketone thujone, from which it may be prepared by reduction by sodium in alcohol. It is identical with the tanacetyl alcohol, originally described by Semmler. It is a liquid, b. p. 92° at 13 mm., and of sp. gr. 0.927. Its ref. index is 1.4635 at 20°. There are probably 3 isomers corresponding to stereoisomeric thujones.

Terpineol, $C_{10}H_{17}.OH$.

Terpineol of commerce is a colourless, strongly refractive, optically inactive liquid of 0.940 sp. gr. at 15°, having a very fragrant odour of hyacinth or lilac-flowers, especially when diluted. By cooling to —50° terpineol yields crystals, m. p. 34° to 35°. Contact with these causes the solidification of terpineol at the ordinary temperature. Terpineol is not attacked by alkalies or fatty acids, and owing to this fact and its high b. p. (218° to 219°) it is extensively employed for scenting toilet soaps.

Terpineol is practically insoluble in water, but dissolves readily in alcohol, ether, hydrocarbons, and fatty oils.

Terpineol is an alcohol the constitution of which has long puzzled chemists. It is now known that there are at least 3 isomeric terpineols of which two at least are present in the terpineol of commerce. A study of the constitution of this alcohol shows that 12 stereo- and other isomers are possible.

Wallach originally prepared a terpineol by acting on terpin hydrate with phosphoric acid. His terpineol boiled at 215° to 218°, and was liquid. By using sulphuric acid, Bouchardat prepared it from terpin hydrate as a solid, m. p. 30° to 32°. Wallach has since shown that this solid variety really melts at 35°. Liquid terpineol of commerce appears to consist of the liquid variety, and of 2 solid isomers, one melting at 35° and the other at 32° to 33°. Semmler has recently prepared optically active terpineols (the ordinary varieties are inactive) by replacing the chlorine in the isomeric limonene hydrochloride by a hydroxyl group. The resulting terpineol is active in the same sense as the limonene from which it is prepared.

Bayer has also synthesised a terpineol, m. p. at 69°.

Terpineol m. p. at 32° (β-terpineol) has a sp. gr. 0.923. It boils at 210° at normal pressure. Its phenylurethane m. p. at 85°. Terpineol, m. p. at 35° to 36°, has a sp. gr. 0.939, and b. p. 219°. Its phenylurethane m. p. at 112°.

Terpineol occurs naturally in several essential oils.

The probable constitutions of the 3 principal isomeric terpineols are as follows:

$$CH_3 \quad CH_2$$
$$CH$$
$$H_2C \diagup \diagdown CH_2$$
$$H_2C \diagdown \diagup CH_2$$
$$C.OH$$
$$CH_3$$
M. p. 32–33°

(or)

$$CH_3 \quad CH_3$$
$$COH$$
$$CH$$
$$H_2C \diagup \diagdown CH_2$$
$$H_2C \diagdown \diagup CH_2$$
$$C$$
$$\parallel$$
$$CH_2$$

$$CH_3 \quad CH_3$$
$$COH$$
$$CH$$
$$H_2C \diagup \diagdown CH_2$$
$$HC \diagdown \diagup CH_2$$
$$C$$
$$CH_3$$
M. p. 35–36°

$$CH_3$$
$$COH$$
$$H_2C \diagup \diagdown CH_2$$
$$H_2C \diagdown \diagup CH_2$$
$$C$$
$$\parallel$$
$$C$$
$$CH_3 \quad CH_3$$
M. p. 69–70°
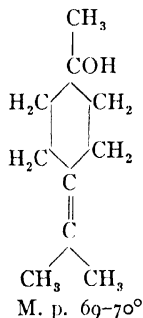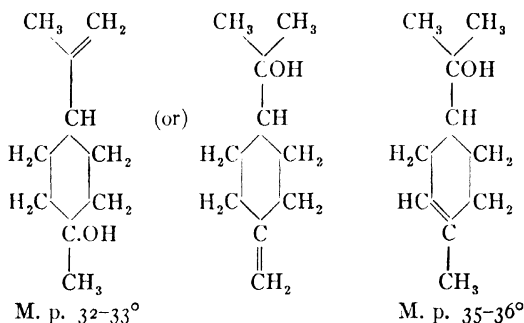
Pulegol, $C_{10}H_{17}OH$.

This, again, is a compound not occurring in nature, but which is obtained by the reduction of the natural ketone, pulegone. It is a viscous liquid, having an odour resembling that of terpineol, of sp. gr. 0.912 and b. p. 215°. It has never been separated in a state of absolute purity, so that its characters are not well defined. An isomer, *iso-*

pulegol, which has been mentioned in connection with citronellal, is formed by the treatment of that aldehyde with acetic anhydrid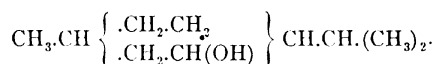e. This alcohol, corresponding with the ketone *iso*pulegone, has a sp. gr. 0.915, and a ref. index 1.4729. It is optically active, $[\alpha]_D$—2.65°, and b. p. 91° at 13 mm.

The ketones are of more practical interest than the alcohols.

Menthol, Menthyl Alcohol, $C_{10}H_{19}.OH$.

Menthol has the constitution of a methyl-isopropyl-phenol hexahydride:

$$CH_3.CH \left\{ \begin{array}{l} .CH_2.CH_2 \\ .CH_2.CH(OH) \end{array} \right\} CH.CH.(CH_3)_2.$$

Menthol occurs, together with menthone[1] and the hydrocarbon menthene, in peppermint oil, and separates in crystals on cooling the oil. The menthol from American oil of peppermint (derived from *Mentha piperita*) usually forms snow-white acicular crystals, or stellate groups of white satiny needles, having the characteristic odour and flavour of peppermint.[2] The product from the Japanese and Chinese oils forms prismatic crystals closely resembling those of magnesium sulphate.

Pure menthol[3] volatilises slowly at the ordinary temperature, m. p.

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[1] Menthone, $C_{10}H_{18}O$; or $CH_3.CH \left\{ \begin{array}{l} CH_2.CO \\ CH_2.CH_2 \end{array} \right\} CH.C_3H_7$. (See p. 191.)

This substance is a ketone which occurs in American oil of peppermint (10 to 12%). It may be prepared by the action of chromic acid mixture on peppermint oil. Menthone is an oily liquid smelling like diluted peppermint oil. Two modifications of it exist, of opposite optical activities, and apparently differing in certain other respects, as shown in the following table:

	Dextro-menthone	Laevo-menthone
Optical activity; $[\alpha]_D$	$+21°(26°$ to $28°)$	$-26°$
Ref. index	1.4528	1.4496
Sp. gr.	0.897 at 20°	0.894
B. p.	206°	208°
Oxime, $C_{10}H_{18}(NOH)$	Liquid; slightly laevorotatory	M. p. 59; laevorotatory.
Amine, $C_{10}H_{19}NH_2$	Liquid; b. p., 206°	Liquid; b. p., 206°.

Laevo-menthone occurs in oil of buchu.

By the action of phosphoric anhydride on the oximes the corresponding *nitriles*, $C_9H_{17}.$-CN, are obtained. From the dextrorotatory variety Wallach prepared the open-chain alcohol *mentho-citronellol*, $C_{10}H_{19}.OH$, isomeric and possibly identical with citronellol.

The *semicarbazone* from dextromenthone, melts at 184°, and has the formula $C_{10}H_{18}:N.$-NH.CONH$_2$.

[2] Chinese and Japanese oils frequently form a semi-solid mass consisting of crystals of menthol saturated with liquid hydrocarbons. According to E. Charabot (*Compt. rend.*, 1900, **130**, 518), the formation of esters appears to be a function of the green part of the peppermint plant, while the oxidation of menthol to menthone is a function of the flowers. This is true of the natural oil; the Japanese oil of comerce has been deprived of much of its menthol.

[3] According to the British Pharmacopœia (1898), menthol occurs in "colourless acicular crystals, usually more or less moist from adhering oil, or in crystalline masses." As pointed

42° to 43°, and b. p. 215.5° (Power). E. J. Parry gives the b. p. of menthol as 212°, and the sp. gr. as 0.890 at 15°.

Menthol is but slightly soluble in water, but imparts to the liquid its characteristic taste and smell. It dissolves readily in alcohol, ether,[1] carbon disulphide, and in fixed and volatile oils. The solutions are lævorotatory; $[a]_D$ = about $-59°$.

Menthol is not soluble in aqueous alkalies, a character which distinguishes it and permits of its ready separation from thymol and phenol.

The proportion of menthol contained in oil of peppermint, etc., is best ascertained by converting it into its acetic ester, as described on page 227.

Menthol is extensively employed as a remedy for neuralgic headache and other affections. It forms the active constituent of the "neuralgic crystals," which, however, are liable to considerable adulteration. Thus, in addition to a legitimate economisation of the menthol by forming the base of the pencil of paraffin-wax, the menthol itself is sometimes mixed with paraffin; and fatty matters, thymol, and other substances have also been added (*Pharm. J.*, [3], **15,** 365, 686). To ascertain the quality of a pencil, a portion of the substance should be scraped from the surface and its m. p. determined. The commercial article fuses at 41° to 43°. An admixture of paraffin-wax notably raises the m. p., unless some other adulterant is also present. On heating a weighed portion of the exterior of the pencil to 100° the menthol will volatilise, and its quantity may be ascertained from the loss in weight, none of the probable admixtures, such as fatty matters, spermaceti, paraffin-wax, salicin, salicylic acid, thymol, etc., being sensibly volatile at 100°. Mineral matters, such as magnesium sulphate, which is said to have been used as an adulterant of menthol, will remain on heating the sample to dull redness in the air.

The ready solubility of menthol in cold 90% is a test of some value, as many adulterants (*e. g.*, paraffin, spermaceti, and fats) are insoluble in that solvent. The alcohol should be heated to boiling

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[1] Waste or impure menthol may be purified by recrystallisation from its solution in ether, benzene, light petroleum, carbon disulphide, or acetone. When ether is employed as the solvent, the menthol crystals can be freed from all foreign odour by a few hours' exposure to the air. (A. W. Gerrard, *Pharm. J.,* 1909, **65,** 163.)

out by Schimmel & Co. (*Report,* Oct., 1898), this description gives official recognition to an impure article. The m. p. of menthol is given as 42°, and ought not to exceed 43°. Menthol is further stated to be "entirely volatilised by the heat of a water-bath, and to acquire an indigo-blue or ultramarine colour when boiled with sulphuric acid diluted with half its volume of water, the acid itself becoming brown." F. B. Power regards this reaction as of "exceedingly doubtful value."

to ensure the complete solution of the menthol, and the liquid then allowed to cool. By operating in this manner the test may be made quantitative.

By reaction with acids, menthol readily yields *esters* and by treatment with phosphorus pentachloride or hydrochloric acid it is converted into *menthyl chloride*, $C_{10}H_{19}Cl$. By distillation with zinc chloride or phosphoric anhydride, menthol is converted into the hydrocarbon *menthene*, $C_{10}H_{18}$, a dextrorotatory liquid which has an odour of cymene, boils at 167°, and combines with bromine to form the addition-product $C_{10}H_{18}Br_4$. This is converted into *cymene*, $C_{10}H_{14}$, by heating and distilling the product with sodium.

Careful oxidation converts menthol into its ketone, menthone. The principal ester is menthyl acetate, a liquid which boils at 224°, and occurs naturally in oil of peppermint.

The reduction of menthone produces a mixture of dextro- and lævo-menthol having an optical rotation of +2°.

It will be convenient to discuss here the indifferent body cineol, which is an oxygenated compound, in which the oxygen does not enter into alcoholic, aldehydic or ketonic functions.

Cineol (Eucalyptol), $C_{10}H_{18}O$.

This compound exists to a very large extent in oils of eucalyptus, wormseed, cajuput, and spike lavender. It is also found to a lesser extent in other oils. It has been described under the names eucalyptol (its most common commercial name) and cajuputol.

Cineol is a product of the action of boiling phosphoric and other mineral acids on terpin hydrate, which is itself readily prepared from turpentine oil.

Cineol is a colourless liquid, having a characteristic camphoraceous odour, and a pungent cooling taste. The sp. gr. of liquid cineol at 15° is 0.930. When exposed to a low temperature, it solidifies to a mass of colourless needles, which melt at −1°. Cineol boils at 176° to 177°. Its ref. index is 1.4596, and it is optically inactive.

Cineol is soluble in all proportions in alcohol, glacial acetic acid, ether, chloroform, benzene, carbon disulphide, and fatty and volatile oils. It is not dissolved by water nor by aqueous solutions of alkali hydroxides. Cineol is itself a solvent of caoutchouc, gutta-percha, benzoic and salicylic acids, phenol, etc.

Eucalyptol,[1] from the oil of *Eucalyptus globulus* or allied species, is now somewhat extensively employed in medicine, the internal dose ranging from 2 to 5 grains. In addition to the characters given above, the alcoholic solution of the commercial article should be neutral to litmus and should not develop a brownish or violet colour on the addition of a drop of tincture of ferric chloride. Such a reaction would indicate the presence of phenols, the amount of which can be ascertained by shaking the sample with an equal measure of N sodium hydroxide, in which cineol is insoluble.

Cineol unites with bromine to form the compound $C_{10}H_{18}O$, Br_2, which crystallises in red needles and prisms that readily decompose into water, bromine, and cinene, half of the last product uniting with bromine to form *cinene tetrabromide*, $C_{10}H_{16}Br_4$.

When cineol is agitated with a strong solution of iodine in potassium iodide, a pasty mass is formed in which green lustrous crystals may be observed. These may be dried partially on a porous plate, but they rapidly deliquesce. The reaction may be employed for the detection of cineol.

By treatment with oxidising agents cineol is readily converted into *cineolic acid*, $C_{10}H_{16}O_5$.

Cineol does not react with phenylhydrazine or hydroxylamine, nor does it combine with bisulphites. It is not affected by sodium or by benzoyl chloride below 120°, but at higher temperatures it yields benzaldehyde, hydrochloric acid, and cinene. When heated with alcoholic sulphuric acid, cineol yields terpinene and terpinolene.

From the foregoing characters it appears that cineol is neither a phenol, a ketone, an aldehyde, nor a true alcohol. The oxygen atom appears to be wholly indifferent. The constitution of cineol is probably that of cinyl oxide, $C_{10}H_{18}$:O, which bears the same relation to terpin that ethylene oxide bears to glycol.

Cineol forms a crystalline compound with iodol, of the formula $C_{10}H_{18}O . C_4I_4NH$, m. p. 112°. It also forms a crystalline compound with resorcinol.

The estimation of cineol or eucalyptol is a matter of considerable importance, as the valuation of eucalyptus oil (and to some extent

[1] Eucalyptol may be conveniently prepared from such of the oils of eucalyptus as contain it by treatment with a strong solution of phosphoric acid (preferably of 1.785 sp. gr.), when a crystalline compound of the composition $C_{10}H_{18}O,H_3PO_4$ separates. This is separated and decomposed by hot water, when the liberated eucalyptol separates as an oily layer, which, after washing by agitation with water, is practically pure. (L. R. Schammel, Brit. Patent, 1894, No. 14138.)

other essential oils) depends entirely on the eucalyptol content.   Early
attempts in this direction were directed to the fractionation of the oil,
and the subsequent freezing out of the eucalyptol.   But such methods
gave but very approximate results and are not now used.   No process
can be said to give absolutely accurate results, so that it is necessary
to state the process used in comparing results obtained by different
observers.

Scammel's process is most generally used.   This consists in care-
fully adding, with continual stirring, to a known weight of the oil,
from 1 to 1.25 times its weight of syrupy phosphoric acid, the oil
being kept cold all the time.   The crystalline magma is pressed be-
tween filter-paper several times in an ordinary letter press, and when
the adherent terpenes and phosphoric acid have been thus removed,
the crystals are decomposed by hot water in a graduated tube, and the
volume of cineol read off.   If the resulting cineol does not crystal-
lise at $-5°$, it is too impure for the estimation to be correct, and must
be repeated.

The U. S. Pharmacopœia recommends that the oil should first
be diluted with petroleum ether.

Schimmel & Co. prefer to absorb the cineol in a Hirschsohn
flask with a 40% solution of resorcinol, and read off the unabsorbed
portion.   This method, however, only gives correct results in certain
cases, and must be regarded as only approximate.

Sesquiterpene Alcohols.

A number of sesquiterpene alcohols of the formula $C_{15}H_{25}OH$
occur in various essential oils, usually those having a high b. p.   They
are frequently solid crystalline compounds, hence they have often
been described as "camphors," a name now obsolete as applied to
such substances.   They are closely related to the sesquiterpenes, and
in nearly all cases are converted into these hydrocarbons by dehy-
dration.   Caryophyllene alcohol, an alcohol corresponding with the
sesquiterpene caryophyllene, however, is an exception; since, although
it is prepared from caryophyllene, it yields a different sesquiterpene,
clovene, on dehydration.

In regard to santalol some doubt exists as to whether it is a true
sesquiterpene alcohol or an alcohol of the formula $C_{15}H_{23}OH$.   At
all events it behaves as a sesquiterpene alcohol and is conveniently
classed with this group.   The principal members are as follows:

Sesquiterpene alcohol	Source	M. p.	B. p.	Other characters	Sesquiterpene
Amyrol.........	West Indian santal oil	Liquid	300°	....	....
Atractylol......	Atractylis oil	Liquid	.....	....	Atractylene.
Cubebol (c u b e b camphor)	Cubebs oil	65° to 67°	248°	Lævorotatory; crystallises in rhombs.	Cubebene (Cadinene?).
Cedrol (c e d a r camphor)	Cedar-wood oil	85° to 86° (Schimmel)	252°	Silky needles; aromatic odour; dextrorotatory	Lævo-cedrene.
Cypress-camphor	Cypress oil	86° to 87°	291°	Long needles; in active	Dextro-cedrene.
Ledenol (l e d u m camphor)	Marsh - t e a oil	104°to 105°	282°	Odourless prisms; sublimes in needles	Ledene.
Patchoulol (p a t - chouli camphor)	Patchouli oil	56°	296°	Lævorotatory; hexagonal prisms	Patchoulene (cadinene?).
Ylang-Ylang camphor	Ylang-Ylang oil	138°	......	....	.. ..
α-Santalol	Santalwood oil	Liquid	300°	Sp. gr. 0.985; rotation — 1° 20′	α-Santalene.
β-Santalol	Santalwood oil	Liquid	310°	Sp. gr. 0.987; rotation − 56°	b Santalene.

PHENOLS AND PHENOLIC ETHERS.

A considerable number of substituted phenols occur as constituents of essential oils. They may be classified in 2 groups, namely, those compounds in which 2 of the hydrogen atoms of the benzene chain are replaced, respectively, by *methyl* and *propyl* or *isopropyl*, and those in which an atom of the benzenic hydrogen is replaced by *allyl* or its isomer *propenyl*. Substitution by ethyl does not seem to occur naturally. In the case of the phenolic ethers of essential oils, the phenolic hydrogen appears to be almost invariably replaced by methyl.

Methyl-propyl Phenols.

Several bodies existing naturally in essential oils have the constitution of *methyl-isopropyl-phenols*. This structure may be regarded as established in the case of thymol and carvacrol. The isomerism of carvacrol and thymol is exhibited by the following formulæ, whence it appears that they are both methyl-isopropyl-phenols.

Carvacrol

$$CH_3$$

OH

$$CH(CH_3)_2$$

Thymol

$$CH_3$$

OH

$$CH(CH_3)_2$$
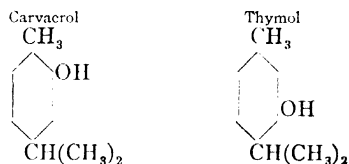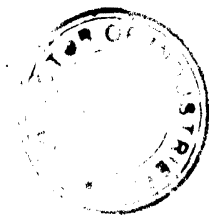
SPECIAL CHARACTERS OF ESSENTIAL OILS.

By HENRY LEFFMANN AND CHARLES H. LaWALL,

In the following section some of the important essential oils are described, and methods for their examination, chiefly with a view to the detection of adulteration, are detailed. The physical characters of oils not described in this section will be found included in a table at end of the volume (p. 431).

Andropogon Oils. Indian-grass Oils.

The oils of citronella, lemon-grass, palmarosa, ginger-grass, and vetiver or cus-cus are all derived from tropical grasses of the genus *Andropogon* (*Cymbopogon*), but there is doubt as to the particular species from which some of the individual oils are obtained.

The table on the following page is compiled from the description of the andropogon oils, given by Parry in *The Chemistry of Essential Oils*, 2d Ed., which should be consulted for further details and much general information respecting them.

Citronella Oil.—The botanical origin and general characters of this oil will be found described in the table on the next page. By far the larger portion of the oil in commerce is produced in Ceylon, by distilling the dry grass (*Lana Batu* or *Maha Pangiri*) with steam. The oil is pale yellow to yellowish-brown, and sometimes greenish owing to traces of copper. The strong odour is pleasant and melissa-like (citronellal).

According to Gildemeister and Hoffmann (*The Volatile Oils*), while the greater part of the oil in commerce is the oil distilled from *Lana Batu* grass, a smaller portion, and that finer and more valued,

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CHARACTERISTICS OF GRASS OILS.

	Botanical origin	Sp. gr. at 15°	Opt. rot.	Ref. index	Chief constituents
CITRONELLA...............	A. (C.) nardus	0.885 to 0.920	0 to − 20°	1.4660 to 1.4800	30% to 50% citronellal; 30% to 38% geraniol.
LEMON-GRASS. Indian verbena. E. I. melissa.	A. (C.) citratus, and A. (C.) flexuosus.	0.895 to 0.905	+ 3 to −3° (often 0)	1.4880	70% to 85% citral.
PALMAROSA. Indian or Turkish geranium.	A. (C.) martini............	0.885 to 0.896	− 2 to + 2°	1.4800	65% to 85% geraniol.
GINGER-GRASS............	(?)	0.935 to 0.942	+ 19 to + 25°	....	Geraniol.
VETIVERT (vetiver, cuscus)......	Root of Vetiveria zizanoides	1.02 to 1.03	+ 25 to + 40°	....	Alcohols and esters.
CAMEL-GRASS.............	A. (C.) saniger, A. (C.) Schœnanthus.	0.905 to 0.919	− 4 to + 34.6°	....	Phellandrene.

is derived from the Singapore and Java grass, *Maha Pangiri*. The following table gives the chief characters and composition of the 2 oils:

	Lana Batu oil	Maha Pangiri and Java oil
Sp. gr. at 15°	0.900 to 0.920	0.886 to 0.900
Op. rot.	—5° to —21°	—0.4 to —3.0
Acetylisable constituents, %	50 to 70	80 to 90
Citronellal, %	28	53
Geraniol, %	33	35
Methyl-eugenol, %	8	0.8

Javanese oil is further stated to contain dextro-citronellol. The high sp. gr. of the Ceylonese oil is due to the greater proportion of methyl-eugenol which it contains.

The solubility of both these citronella oils is the same, a clear or only faintly opalescent solution being formed on shaking with 1 to 3 volumes of 80% alcohol. When this clear solution is diluted to 10 volumes with 80% alcohol, no oily drops should separate on standing, though a mere turbidity may be disregarded if previously present. This is known as "Schimmel's test" (see page 305).

In order to avoid any uncertainty as to the indications given by Schimmel's test, Parry (*Chem. and Drug.*, 1901, **59**, 142) has proposed the use of a slightly stronger alcohol in the case of those oils which give a turbidity with 80% alcohol. Some pure oils (generally those of high sp. gr.) give a clear solution with 3 or 4 vols. of 80% spirit, and subsequently a turbid solution on diluting to 10 volumes. In nearly all such cases the use of alcohol of 81 to 83% strength results in a clear solution with 10 vols. of the alcohol. If small quantities of petroleum are present, however, there is little change in the turbid solution even if 85% spirit be employed.

Umney and Swinton have published results showing that the variable composition of commercial citronella oils is probably, at least in part, due to the fact that some distillates are produced by the aid of steam and others by the open-fire method (*Year Book Pharm.*, 1897, 365).

Citronella oil contains, as its chief constituents, citronellal and geraniol. The terpenes camphene and dipentene, and probably limonene, constitute about 10 to 15% of the oil. Methyl-eugenol, lævoborneol

(1 to 2%), methyl heptenone, linalol, and acetic and valeric esters, 2 sesquiterpenes, and possibly terpineol also occur in citronella oil.

The methods for the estimation of citronellal and geraniol are fully described on page 270 *et seq.* The acetylation process when applied to citronella oil does not express the true proportion of geraniol, as is now generally recognised (p. 270). But it does give a *relative* figure, and the acetylisable constituents should always be estimated.

Citronella oil is much used as a perfume for cheap toilet soaps, and in consequence is frequently adulterated. Petroleum (kerosene) is much employed, and fixed oils are sometimes added. Either adulterant disturbs the ready solubility of the oil in 80% alcohol, petroleum producing a milk-white mixture and after long standing oily drops on the surface of the solution; fixed oils cause a turbid liquid, and eventually oily drops collect at the bottom. Another difference is that a citronella oil containing fixed oil is not soluble in 80% alcohol in any proportion (1 to 10 volumes), oils containing petroleum are soluble in 2 volumes, but with 10 volumes the milk-white turbidity is produced.

Parry and Bennett have recorded the presence of 20% of alcohol in citronella oil. The oils containing this also contained other adulterants, the spirit being added to enable the samples to meet Schimmel's test. Gurjun-balsam oil has been found in adulterated oil of citronella.

One of the recently discovered adulterants is *light resin spirit* found by Parry and Bennett to the extent of 12% and upward in certain oils (*Chem. and Drug.*, 1903, **62**, 88, 408). Although the exact nature of this adulterant is somewhat doubtful, Parry and Bennett believe it to be either pure light resin spirit or a mixture of this substance with light petroleum spirit. On fractional distillation at reduced pressure (20 mm.), such adulterated oils gave a fraction (first 10%) having a sp. gr. of 0.822, a rotation of $-26.8°$, a ref. index of 1.4490, and b. p. 150° to 160° at the ordinary pressure. Under similar conditions, Parry and Bennett found normal citronella oils to give a fraction having a minimum sp. gr. of 0.858; opt. rot., $-45°$ (but this is variable); ref. index, near 1.4600, and not below 1.4570 at 20°. The solubility of the fraction in 10 volumes of 80% alcohol should be noted. Pure oils always yield a perfectly soluble fraction, but oils containing notable proportions of resin spirit yield an insoluble fraction. These characteristics, and the reduced rotation of the first 10% distilled, are stated by Parry and Bennett to suffice for detection of the adulterant.

For some time Schimmel's test (p. 305) was regarded as sufficient to detect all likely adulterants, but the discovery of light petroleum and resin spirits in citronella oils was shown by Parry and Benett to place the test in a less satisfactory position. Thus while some of these adulterated oils give distinct insoluble matter with Schimmel's test, others have been found to contain 20% of the resin-spirit and yet meet the test. For this reason Schimmel & Co. have described the following modified test (the so-called "Raised Schimmel's test"): 2 tests are made side by side: one exactly as usual in the ordinary Schimmel's test; the other after the addition of 5% of Russian petroleum to the oil under examination. Both the original oil and that to which petroleum has been added should be soluble in 80% alcohol as employed, and oily drops should not separate in either case.

The following standards have been suggested by Parry and Bennett for citronella oils (*Chem. and Drug.*, 1903, **62**, 999). The limits of sp. gr. and opt. rot. apply only to normal Ceylon oils, and not to East Indian distillates:

Sp. gr. at 15.5°...................	0.900 to 0.915
Opt. rot.......................	0° to −15°
Sp. gr. of first 10% distilled (at 20 to 40 mm.).	Above 0.858
Ref. index of first 10% (at 20°).......	Above 1.4570
Solubility of oil in 80% alcohol........	To pass Schimmel's test.
Geraniol and citronellal (acetylation method, as total geraniol)...........	Above 58%

Lemon-grass Oil.—This oil is obtained by distilling the fresh grass, *Andropogon (Cymbopogon) citratus, C. flexuosus*, the yield being from 0.24 to 0.4%. (See table on page 304 for further particulars and general characters of the oil.) (See page 447.)

Lemon-grass oil is yellow to brownish-red, with a strong odour. The majority of Ceylon and Cochin China oils have a sp. gr. between 0.895 and 0.905, and opt. rot. lying between the limits of +3 to −3°. Ceylon and Cochin China oils, when freshly rectified, dissolve to a clear solution in 2 to 3 parts and more of 70% alcohol, but are slightly less soluble after 3 months. Certain lemon-grass oils having characters outside all these limits are met with. Thus West Indian lemon-grass oil is an oil of fine odour, of sp. gr. from 0.877 to 0.887, and containing from 75 to 85% of aldehyde. Cameroon oils have a sp. gr. about 0.885 and may contain 78% of citral.

Lemon-grass oil consists largely of citral, which occurs up to 85%.

In addition, methyl-heptenone, geraniol (partly as esters), and possibly linalol, dipentene and limonene (10% of terpenes) are present, together with small amounts of citronellal and traces of cymene, normal decyl aldehyde, and possibly traces of another aldehyde isomeric with citral.

The estimation of citral in lemon-grass oil is described at length on page 270 *et seq.* The sulphite method is useful only as giving comparative results between various samples, the figures not being absolutely accurate. The presence of methyl-heptenone does not interfere with the estimation of citral by this method, since the compound formed with this ketone is decomposed at 100° and the free ketone is measured with the unabsorbed portion of oil.

Lemon-grass oil should contain not less than 70% of citral. Many samples contain a much larger proportion, but some have suffered partial extraction of this constituent. This oil is frequently adulterated, and some of the additions made to increase the value (for instance, *acetone*, found by Parry) are ingenious. Fixed oils are often added and occasionally petroleum. Either of these latter additions cause a decreased solubility in 70% alcohol, while the sp. gr. is generally disturbed.

Citronella oil was found by Parry in certain consignments of lemon-grass oil. The solution of the oil in 70% alcohol quickly became cloudy on cooling, pure oils requiring somewhat prolonged cooling of this solution to produce cloudiness. Citronellal was readily detected in the sulphite compound separated from the oil.

Acetone was found by Parry in some lemon-grass oils of slightly low sp. gr. (0.893). The apparent percentage of citral was 76. Distillation of such oils at the ordinary pressure gave about 11% of distillate (chiefly acetone) below 60°.

Lemon-grass oil is used in perfumery, and has been employed in the adulteration of lemon oil. An important use to which it is now put is in the manufacture of *ionone*, the artificial perfume of the violet produced from lemon-grass citral.

Another volatile oil possessing a lemon-grass-like odour is derived from the leaves of a small tree (*Backhousia citriodora*) growing in southern Queensland. It contains a larger proportion of citral than lemon-grass oil, yielding as high as 94.95%, according to Umney. This oil should not be confused with the oil from *Eucalyptus citriodora*, which contains little or no citral, but consists almost entirely of citronellal.

Palmarosa Oil.   Indian Geranium Oil.—This oil, ·sometimes misnamed Turkish geranium oil, is pale and dark yellow according to the method of distillation.   It has a characteristic geranium or rose-like odour, and contains a large proportion of geraniol, chiefly free, but from 5 to 15% of esters (geranyl acetate and caproate) are generally present.   In addition, it contains a small quantity of dipentene, and possibly some methyl-heptenone.   The free geraniol present ranges from 65 to 85% in pure oils, as determined by acetylation, while the total geraniol should not be less than 75% and frequently reaches a much higher figure (93%).   The esters present absorb from 3 to 5% of potassium hydroxide.

Schimmel & Co. give the following percentages of geraniol in 4 pure samples:

	Combined	Free	Total
1	12.1	76.36	88.46
2	13.55	69.93	83.33
3	8.67	68.23	76.9
4	8.48	83.15	91.63

Pure palmarosa oil has sp. gr. 0.885 to 0.896.   It is but slightly active optically, the range noted being −2° to +4°.   Ref. index is about 1.4800.

The oil should dissolve to a clear solution in 3 volumes of 70% alcohol.   Many adulterants interfere with the solubility of the oil, among which are the oils of gurjun balsam and turpentine, and petroleum, fixed oils (especially coconut oil) and cedar-wood oil. Fixed oils .leave a non-volatile residue.   The ester value and geraniol content are lowered by oil of turpentine, which also lowers the sp. gr., as does petroleum.   Oils containing an admixture of coconut oil frequently partially solidify in a freezing-mixture.

Palmarosa oil is not related to true geranium oil in any way, but it possesses a similar odour.   It is employed in cheap perfumery, and finds use also as an adulterant of rose otto and of true geranium oil. It is known locally as "Rusa" oil.

Oil of ginger-grass (table p. 304) was formerly regarded as adulterated or inferior palmarosa oil, but it is now known to be a distinct product, although its source has not been identified botanically.

Angelica Oil.

This oil is present in all parts of the herb *Angelica officinalis* (*Angelica Archangelica*), but is mainly distilled from the roots. According to Schimmel & Co., however, the finest oil is that distilled from the fruit (seed).

Angelica-root oil, when distilled from the fresh material, is light yellow or reddish with an aromatic odour and a pungent taste. By exposure to air and light, it becomes of a yellow or brownish colour, and on long standing the oil deposits a crystalline substance. Giordani found this compound to melt at 74° to 77°, and to have the composition $C_{22}H_{62}O_5$. The ref. index of the oil is about 1.4800.

The following table shows the properties of angelica oil, according to the character of the plant used for distillation:

Material used	Sp. gr. of oil at 15°	opt. rot.	Constituents
Fresh root...............	0.854 to 0.905	+18 to +36°	Methyl-ethyl-acetic acid; dextrophellandrene; oxypentadecylic acid.
Dried root............ ..	Up to 0.918	....	....
Whole herb.... . ..	0.869 to 0.890	+8 to +25°	....
Fruit (seed)...	0.856 to 0.890	+10 to +13°	Phellandrene; methyl-ethyl-acetic acid; oxymyristic acid.

3 samples of angelica-root oil examined by Haensel showed sp. gr. of 0.854 to 0.856 and opt. rot., +38° to +39°. An oil from the dried root had a sp. gr. of 0.875, and an opt. rot. of +23.6°.

It was shown by Beilstein and Weigand in 1882 (*Ber.*, 1882, **15,** 1741), and by Naudin in 1883 (*Bull. Soc. Chim.*, [2], 1883, **39,** 406), that oil of angelica-root contained terpenes, of which dextrophellandrene has since been recognised by Schimmel & Co. (*Rep.*, April, 1891). The oil (root-oil?) distils, according to Parry, between 170° and 310°. Pinene and cymene are possibly also constituents of this oil and the presence of one or more sesquiterpenes has been inferred from the high b. p. (250°) of the heavier fractions.

Ciamician and Silber (*Ber.*, 1896, **29,** 1811) have isolated from angelica-root oil 2 crystalline substances, which are stated to have the constitution of anhydrides of oxyacids. Angelica oil also contains methyl-ethyl-acetic acid and oxypentadecylic acid, $C_{15}H_{30}O_3$, the latter substance crystallising from ether in groups of needles, m. p. 62° to 63°. As has been pointed out by Schimmel & Co., it is worthy

of note that the oxypentadecylic acid present in angelica-root oil is replaced by oxymyristic acid, a lower homologue, in the oil from angelica-fruit. Angelica-root oil finds its chief employment in the manufacture of liqueurs.

Japanese angelica-root oil is the product of the plants *Angelica anomala* and *A. refracta.* The sp. gr. of the oil is about o.910 at 20°. It has an acrid odour, but resembles musk to some extent. At a temperature of 10°, crystals separate from the oil, which solidifies to a pasty mass at 0°. These crystals melt at 62° to 63°, and have all the characters of a fatty acid, possibly oxypentadecylic acid.

The b. p. is between 170° and 313°, the high-boiling fractions are bluish-green.

Anise Oils.

True anise oil is obtained from the fruit of *Pimpinella Anisum.* The oil of star-anise, obtained from the fruit of *Illicium verum*, constitutes the bulk of the oil of anise found in commerce. Both oils are recognised in the British Pharmacopœia (1898) and in the United States Pharmacopœia (8th Rev.). An oil produced from *Seseli Harveyanum*, known in some parts of Australia as "anise oil," has more of the appearance and flavour of fennel oil.

Anise oil (from *Pimpinella Anisum*) contains anethol, methyl-chavicol and possibly aniseketone, with small quantities of anisic aldehyde and anisic acid. W. A. Tilden states that dextropinene is also present. In addition to these constituents, oil of star-anise contains dextropinene, lævophellandrene, safrol, and the ethyl-ether of hydroquinone. According to Tardy, terpineol is also present.

Bouchardat and Tardy (*Ct. r.*, 1896, **122,** 198) found a sample of Russian anise oil to contain small quantities of aniseketone and fenchone. The sample examined by them, however, was not a normal oil, since it had a m. p. of 10° and was dextrorotatory. It is most probable, therefore, that the sample in question was adulterated with fennel oil.

The *physical characters* of the 2 forms of anise oil are practically identical. Both are pale yellow and somewhat viscous. The British Pharmacopœia (1898) directs that it should congeal when stirred at temperatures between +10° and +15°, and should not become liquid again below +15°. The sp. gr. at 20° should be 0.975 to 0.990. The United States Pharmacopœia (8th Rev.) gives the sp. gr. at 25°

as 0.975 to 0.985; the ref. index, 1.554 to 1.560. A normal oil should
not melt at a temperature lower than +15°, the usual range be-
ing about +15° to +18° or 19°. The m. p. is determined in the
following manner: A small quantity of the oil contained in a narrow
test-tube is first immersed in a freezing mixture. A trace of crystallised
oil of anise may be added to accelerate crystallisation. The tem-
perature is then slowly raised, a thermometer with its bulb immersed
in the oil being used as a stirrer. The oil should not become liquid
below 15°. Care should be taken that the sample is well mixed before
using a portion for the determination of the m. p.

It is necessary to observe the m. p. of the solidified oil, since the
solidifying-point is rendered useless by the fact that anise oil has a
tendency to remain liquid below its true congealing-point (J. C.
Umney, *Pharm. J.*, [3] 1889, **19,** 648). If the solidified oil has a m. p.
below 15°, the sample has either suffered admixture with some foreign
oil, or a portion (or the whole) of its anethol has been removed. The
United States Pharmacopœia, however, directs that the *congealing-*
point of anise oil be observed as described, the highest temperature
obtained during the solidification being noted as this point, which
should not be below 15°. According to Pancoast and Kebler (*Amer.
J. Pharm.*, 1901, **73,** 356), pure anise oils having a low congealing-
point are sometimes met with. They are obtained from a mixture of
natural and artificially ripened seeds, and are known as "Flower Oils."
According to the United States Pharmacopœia (8th Rev.), absence
of oils containing phenols may be proved by the following tests: An
alcoholic solution of the oil should be neutral to litmus-paper, and
should not assume a blue or brownish colour on the addition of a drop
of ferric chloride test solution. The absence of alcohol is shown by
shaking a definite measure of the oil with water in a narrow cylinder.
Spermaceti is said to have been used as an adulterant of anise oil. If
present in notable amount, spermaceti would lower the sp. gr. and
raise the m. p. The solubility of the oil in alcohol would also be
reduced. Pure anise oil should dissolve to a perfectly clear solution
in 3 parts of 90% alcohol. Oxidised oils are more soluble, completely
oxidised samples dissolving in rectified spirit in all proportions.

The presence of methyl-chavicol, the isomer of anethole, in anise
oil, is shown by the action of boiling alcoholic potassium hydroxide on
the anethol-free oil. The b. p. of the liquid is raised, and on cooling,
a further large quantity of anethol crystals is produced.

The constituents of oil of anise gradually undergo oxidation on keeping the oil, a rise in its sp. gr. being produced, while the m. p. is lowered. Oxidised oils show the presence of notable quantities of anisic aldehyde when shaken with sodium hydrogen sulphite solution (25%), whereas fresh oils give no such reaction. Oils examined by this test should be kept at 20° to prevent crystallisation of anethole.

Estimation of Anethole.—The value of oil of anise depends upon its contents of anethole. The proportion of this constituent may be approximately estimated by cooling the oil to a low temperature, and after crystallisation has taken place, pressing the crystals between blotting-paper, and weighing the anethole thus obtained. The amount of anethole may also be ascertained by fractionally distilling the oil, and collecting the fraction coming over between 225° and 235° separately (anethole boils at 232°). The measure of this fraction corre sponds very nearly to the content of anethole. Good samples of anise oil generally contain at least 85% of anethole, and the amount should not be less than 80%.

The 2 oils are slightly lævorotatory, usually about —1° to —3°. This figure is a valuable indication of the purity of anise oils, since their adulteration with fennel oil (or its stearoptene) causes them to show dextrorotation. According to E. Dowzard, some samples of pure anise oil show slight rotation, from +0.03° to +0.7°. This is due to the presence of fenchone, which in the case of adulteration with the stearoptene of fennel oil is retained to a sufficient extent in the stearoptene to cause the product to be more or less dextrorotatory, according to the amount of adulterant present.

Petroleum is sometimes added to anise and star-anise oils. This adulterant causes the oils to be less soluble in alcohol, and lowers the sp. gr., but the m. p. will not be greatly modified. For the estimation of petroleum, the oil may be heated with concentrated sulphuric acid. A residue so obtained consists of petroleum. J. C. Umney found from 37 to 56% of this adulterant in anise oils. The separated petroleum had a sp. gr. of 0.835.

J. C. Umney (*Chem. and Drug.*, 1899, **54**, 323) considers that the differences in the physical characters of star-anise oils are caused by distillation from raw materials, oils in some parts of China being produced from the leaves and twigs of the star-anise. Parry (*Chemistry of Essential Oils*) favours the view that the differences observed in the commercial oils of anise are not due to the cause des-

cribed by Umney, but to the fact that the flowers or very early fruits of
the plant (removed to allow the remaining fruits to mature to better
advantage) are distilled, yielding an oil containing a lower percentage
of anethol.   Parry examined an oil of this description with the follow-
ing results: Sp. gr., 0.9916; rotation, +0.3°; solidifying-point, 12°.
Umney found that the oil distilled from the leaves had a sp. gr. of
0.9878, and a rotation of +1°.   The oil, however, remained fluid even
at 8°.   By fractional distillation, the oil was found to be rich in anise
aldehyde, which usually only occurs in partially or wholly oxidised oils
of anise and star-anise.   It is probable that the presence of anisic alde-
hyde in star-anise oil is the cause of the difference in odour between oil
of anise and star-anise.

The oils of anise are said to be distinguishable by the following
colour test: A saturated solution of hydrochloric acid gas, when added
to the oil, gives with anise oil a deep blue, and with star-anise oil, a
yellow or brown.

According to J. C. Umney, the so-called "Australian anise oil" has
a sp. gr. of 0.914, and an opt. rot. of +14°.   It does not become crystal-
line at 4°.   The oil appears to resemble fennel oil more than ordinary
oil of anise.

The physical constants and characters of other unimportant varieties
of anise oil are described in the table on page 433.   A false aniseed
from *Illicium religiosum* has been found to yield an oil with a sp. gr. of
1.006, containing eugenol, cineol, safrole, and several terpenes.   A so-
called anise-bark oil possesses a sp. gr. of 0.969, and consists chiefly
of methyl-chavicol.

Bay Oil.

This oil, which has frequently been described as being obtained from
the leaves of *Myrcia acris*, is, according to E. M. Holmes *(Pharm.
J.* [3], 1891, **21,** 837), the product of *Pimenta (Eugenia) acris*.
Both the fresh and the dried leaves have been employed in the
distillation of this oil.

Oil of bay is not official in the British nor the United States Pharma-
copœia, but was in the 7th revision (1890) of the latter.   The sp. gr.
of the oil ranges from 0.965 to 0.985, being usually about 0.970.
Parry *(Chemistry of Essential Oils)* gives the normal sp. gr. of the oil
as from 0.965 to 0.995.   Oils of higher sp. gr. should be regarded
with suspicion, being possibly adulterated with oil of pimento or cloves.

The rotation of bay oil should not exceed $-2°$. Adulteration with oil of turpentine will alter this figure considerably.

Mittmann (*Arch. Pharm.*, 1889, **237**, 529) found bay oil to contain pinene, dipentene, eugenol, and methyl-eugenol. In a research by Power and Kleber (*Pharm. Rund.*, 1895, **13**, 60), the presence of Mittmann's terpenes was not confirmed, although lævophellandrene was found in the oil. Power and Kleber also recognised the following substances as being constituents of bay oil: Eugenol, methyl-eugenol, chavicol, methyl-chavicol, citral, and "myrcene," an open-chain hydrocarbon of the formula $C_{10}H_{16}$, which distilled over between 67° and 68° at 20 mm. pressure, and had the sp. gr. 0.8023.

Bay oil suffers adulteration with several oils, chiefly those of cloves pimento, and turpentine. Clove and pimento oils may be detected by the high sp. gr. and by the following test, directed by the United States Pharmacopœia (1890): If to 3 drops of the oil contained in a small test-tube 5 drops of concentrated sulphuric acid are added, and after the tube has been corked, the mixture allowed to stand for 30 minutes, a resinous mass will be obtained. On adding to this mass 4 c.c. of diluted alcohol, vigorously shaking the mixture, and gradually heating to boiling, the liquid should remain nearly colourless, especially not becoming a red or purplish-red.

Turpentine oil, when present as an adulterant, may be detected in the first fraction of the distilled oil of bay by means of the nitroso-chloride reaction for pinene (page 167) which, according to Power and Kleber, is not present in pure bay oil.

When freshly distilled, bay oil is easily soluble in 90% alcohol. On keeping, its solubility becomes slightly lessened.

The phenolic constituents of bay oil (eugenol and chavicol) are present in considerable proportion, and an estimation of them is valuable. For this, Thoms' process, as described on page 295, is perhaps the most accurate. By this method the proportion of phenolic constituents in genuine bay oil ranges from about 59 to 65%.

Schimmell & Co. report two samples from the Fiji Islands with phenol content of 23% and 24%, respectively, due probably to some manipulation in the manufacture. (*Report*, Oct., 1909, **27**.)

Bay oil finds its chief employment in perfumery, notably in the manufacture of bay rum.

California bay oil is in every respect different from the true oil of bay. The Californian oil is obtained by the distillation of the leaves of

Umbellularia (Oreodaphne) californica, a tree commonly known as the mountain-laurel, sassafras laurel, or Californian olive tree. The oil is a light yellow liquid, sp. gr. of 0.930 to 0.950 (Parry, *Chemistry of Essential Oils*). According to Heaney (*Amer. J. Pharm.*, 1875, **47**, 105), the oil contains a hydrocarbon of sp. gr. 0.894 and b. p. 175°. The oil appears to contain cineol.

The sweet bay, *Laurus nobilis*, yields an essential oil having a specific gravity of 0.920 to 0.930 and an optical rotation of −15° to −18°. This oil is found in both the leaves and berries. It contains pinene, cineol, traces of eugenol, probably methyl-chavicol and small amounts of acetic, isobutyric, and valeric acids.

Bergamot Oil.

This oil is obtained by expression of the fresh peel of the ripe fruit of *Citrus bergamia*. It is greenish, has a pleasant odour and bitter taste. Rectification deprives the oil of its tint, but the product thus produced is much inferior in quality to the undistilled, the esters being considerably reduced in amount (12 to 15% or less).

The green tint is probably due to chlorophyl. Gildemeister and Hoffmann, however, state that the copper is the cause (*The Volatile Oils*, 473).

The sp. gr. ranges from 0.882 to 0.886, and in some seasons to 0.888. The distilled oil has a sp. gr. of 0.870 to 0.880. The undistilled oil has a rotation of +8° to +22°, but rarely over +18. Many oils are too dark for observation in the 100 mm. tube, and a shorter tube must be employed. The ref. index lies between 1.465 and 1.466.

Freshly expressed oil of bergamot deposits a white, odourless, and tasteless substance known as *bergaptene*. Bergaptene crystallises in needles having the composition $C_{12}H_8O_4$, and melting at 188°. It is the methyl-ether of a dioxycoumarin, or the inner anhydride of bergaptenic acid. On fusing bergaptene with potassium hydroxide, phloroglucol is formed. According to Soden and Rojahn, bergaptin, a body melting at 59°, is also present in the oil. In addition to these solid constituents, bergamot oil contains dextrolimonene; dipentene (?); linalol; and linalyl acetate (30 to 42%). Octylene, pinene, camphene, and acetic acid are also said to be present. The odour is much richer than is that of linalyl acetate alone, and therefore other

odoriferous constituents, as yet unknown, exist in the oil. Bergamot oil gives no reaction with Schiff's reagent; unlike orange and lemon oils, it contains no aldehydic body.

According to Charabot (*Bull. Soc. Chem.*, [3], 1899, **21,** 1083), the linalol first produced in the fruit is largely converted into ester, during ripening, by the free acetic acid present, while a small amount of the alcohol is dehydrated, producing terpenes. Schimmel & Co. have shown that the proportion of linalyl acetate increases as the fruit ripens. The following figures illustrate this (*Rep.*, April, 1896): Oil from unripe fallen fruits, 25% esters; from unripe plucked fruits, 33 to 34%; from average ripe fruits, 37%; and from somewhat over-ripe fruits, 44% of esters (linalyl acetate).

Most genuine oils show an ester-content of from 35 to 42%. Some pure oils occasionally contain only 30% of linalyl acetate, but this low figure should be regarded with suspicion. Within limits, the value of the oil, which is chiefly used for perfumery, depends upon the percentage of esters it contains. For this reason, it is important to bear in mind that the presence of fatty oils and resins (colophony, etc.), adulterations frequently practised, will increase the apparent content of esters.

The presence of the waxy constituents in bergamot oil (bergaptene, etc.) causes it to leave a considerable residue on evaporation at 100°, which residue, in the case of genuine oils, ranges from 4 to 6%. A known weight of the oil (say 2 grm.) is heated at 100° until the odour has completely disappeared. The residue is cooled and weighed. Published analyses show that this residue always contains a small amount of linalyl acetate (1 to 2%). If more than 6% of residue remains, the sample is probably adulterated, and should be examined for the presence of fatty oils and resins by ascertaining the saponi-fication-value. A soft, green, homogeneous residue, not exceeding 6%, is obtained in the case of genuine oils. When pure the oil is usually soluble in half its volume of 90%, and in 2 volumes of 80%, alcohol. The presence of fatty oils (except castor oil) interferes with this solubility.

Besides adulteration with fatty oils and resins, bergamot oil suffers adulteration from oils of turpentine, lemon, and orange, and from distilled bergamot oil (obtained by rasping the peel of injured fallen fruits and distilling the product with water). Oils of turpentine, lemon, and orange decrease the sp. gr. solubility, fatty residue, and the pro-

portion of esters, while lemon and orange oils raise the opt. rot.   The
sp. gr. is increased, on the other hand, by the addition of fatty oils,
cedar-wood oil, and gurjun balsam.   Synthetic esters and lemon
terpenes are frequently added together to bergamot oils.   An addition
of distilled bergamot oil lowers the ester-content and the residue non-
volatile at 100°.   Fractional distillation should be carried out on all
oils suspected to contain oil of turpentine and added terpenes.

S. Gulli (*Chem. and Drug.*, 1901, **59**, 383) has described a new
adulterant of bergamot oil, which is prepared by treating oil of tur-
pentine with hydrochloric acid gas to saturation (pinene hydrochlo-
ride?).   This preparation can be added to bergamot oil to the extent
of about 10% without materially altering the constants of the oil or
interfering greatly with the ester-value (1 to 2% lower).   Gulli
recommends that in the case of doubtful samples, several grm. of the
oil be saponified with alcoholic potassium hydroxide, the liquid
evaporated to dryness and the residue ignited.   The aqueous solution
of the residue should then be tested for the presence of chlorides with
silver nitrate.

An inferior oil is obtained from the peel of unripe or damaged
fruit.   It is brownish-green, has not a very fragrant odour, and
contains about 20 to 25% of esters.   A sample examined by G. Fabris
showed 25.5% of linalyl acetate, and had a sp. gr. of 0.885; optical
rotation at 20°, +9.5°; residue at 100°, 2.70%, containing 1.75%
of linalyl acetate.

Oil of bergamot leaves is rarely obtained pure.   It is sometimes
used as an adulterant of orange oils.   It has a sp. gr. of 0.882 to 0.886,
a rotation of +8° to +22°, ref. index 1.4654 to 1.4660, and is soluble
in an equal volume of 90% alcohol.   It contains 32 to 34% of esters
(calculated as linalyl acetate), including methyl anthranilate.

The so-called *oil of wild bergamot* (from *Monarda punctata* and *M.
fistulosa*) is stated by Braudel and Kremers to contain thymoquinone
and hydrothymoquinone.   In addition, the oil from *M. punctata*
contains cymene, thymol, and dextrolimonene; while that from *M.
fistulosa* contains cymene, carvacrol, and limonene.

Cajuput Oil.

This oil is official in the British Pharmacopœia (1898) and in the
United States Parmacopœia (8th Rev.), and is distilled from the
leaves of *Melaleuca leucadendron*.   Many other species of this plant

produce oils very similar to the official oil (*e. g.*, *Melaleuca minor*, *M. uncinata*, *M. acuminata*, *M. viridiflora*, etc.

The British Pharmacopœia describes cajuput oil as bluish-green, with an agreeable, penetrating, camphoraceous odour, and an aromatic, bitter camphoraceous taste. It has a sp. gr. of 0.922 to 0.930. The oil should become semi-solid on being stirred, when cold, with 1/3 or 1/2 its volume of phosphoric acid (of sp. gr. 1.75). This test ensures the presence in the oil of a due proportion of cineol.

The U. S. Pharmacopœia (8th Rev.) describes cajuput oil as having a sp. gr. of 0.915 to 0.925 at 25° and being soluble in 1 part of 80% alcohol. The oil should be lævorotatory (not more than −2°) and should be free from *copper*. It should contain at least 55% of cineol (by volume) when assayed by the phosphoric acid process, the phosphate being decomposed by warm water and the resulting cineol measured (see page 339).

Some foreign pharmacopœias (*e. g.*, Italian and Japanese) allow a lower limit than 0.922. The average cajuput oil differs very little from the British Pharmacopœia limits, although of recent years the sp. gr. of many pure oils has slightly decreased (to 0.918) owing to a lowered cineol content. Cajuput oil oxidises on exposure to air, the small quantities of butyric, valeric, and benzoic aldehydes being converted into the corresponding acids. The slightly acid reaction of crude cajuput oil is probably due to saponification of the terpenyl acetate and to the above-mentioned oxidation of the aldehydes. Exposure of the oil to light causes polymerisation.

The ref. index of cajuput is of about 1.4650 to 1.4680, and normally contains up to 65% cineol.

The sp. gr. of cajuput oil is lowered by adulteration with turpentine oil. Oils containing less than the normal amount of cineol will also show a low sp. gr.

The bluish-green of cajuput oil is chiefly due to traces of copper. The rectified oil is colourless.

Cineol (eucalyptol) is the chief constituent; terpineol, terpinyl acetate, and 1 or more terpenes are also present. The varieties differ in certain respects from each other in properties and composition. Some (*M. leucadendron*, etc.) contain several fatty compounds, such as butyric and valeric aldehydes. Bertrand (*Bull. Soc. Chim.* [3], 1893, **9,** 432) found that *M. viridifolia* gave an oil (known as "Essence of Niaouli") similar in odour to cajuput oil, and containing cineol,

terpineol, valeric and benzoic aldehydes, valeric acid and terpineol
valerate, dextropinene and lævolimonene, methyl salicylate, and a
sulphur compound.

Cajuput oil is generally slightly lævorotatory, ranging from 0° to
−3°. The oil from *M. acuminata*, however, is stated to have an
optical rotation of −15°.

Cineol is best estimated by the process described on page 339.
Oils of good quality yield 60 to 65%, and 50 to 55% should be fixed as
the minimum limit. As already stated, the United States Pharma-
copœia requires cajuput oil to contain at least 55% by volume of
cineol. Eucalyptus oil is sometimes added to cajuput oil which
has been deprived of a portion of its cineol. Oil of good quality
should give 60% of distillate between 175° and 185°.

The following characters of the oils from several species of *Mel-
aleuca* are given by Parry (*Chemistry of Essential Oils*):

	Sp. gr.	B. p.	Opt. rot.
M. decussata	0.938	183 to 209°	....
M. ericifolia	0.899 to 0.902	149 to 184°	+26°
M. linarifolia	0.903	175 to 187°	+11°
M. Wilsonii	0.925	....	....
M. uncinata	0.925	175 to 180°	+1.7°
M. leucadendron (*var. lancifolia*)	0.955	....	−3.6°
M. acuminata	0.892	....	−15.3°
M. thymifolia	0.9134	172 to 214°	....

Camphor Oil.

Camphor oil is a liquid occurring with camphor, and obtained as a
secondary product in the extraction and refining of that compound.
The method of manufacture as carried out in Japan has been de-
scribed by H. Oishi (*Chem. News*, 1884, **50**, 275), who states that
the crude camphor oil (sp. gr. 0.959) obtained by pressing the
semi-solid mixture of camphor and oil (from the distillation of the
wood with steam) still contains a considerable amount (20 to 30%)
of solid camphor which can be recovered by fractional distillation.
On distillation, the crude camphor oil gave 6% over below 150°, about
24 between 150° and 170°, 38 between 170° and 180°, and 19.0%
between 180° and 198°, leaving a residue in the retort of 13%. The

camphor oil thus purified is described by Oishi as a colourless liquid which gradually turns yellow by exposure to air and has a sp. gr. of 0.895.

P. MacEwan, writing in 1885 (*Pharm. J.* [3], 1885, **15,** 1045), states that Borneo camphor oil from *Dryobalanops aromatica* differs from the oils from Formosa and Japan in not undergoing any change on exposure to a low temperature. MacEwan found that if 2 c.c. of nitric acid of 1.42 sp. gr. were allowed to act on a few drops of Japanese camphor oil for 1 minute, and the mixture was then diluted with 2 c.c. of water, the clear, aqueous liquid became crimson, whereas Formosa oil when similarly treated gave a milky solution having a scarcely perceptible green shade. MacEwan suggests the coloration produced on treating Japanese camphor oil with nitric acid as a means of detecting its presence in oil of wintergreen, said to be adulterated with it in the United States.

H. Yoshida (*J. Chem. Soc.*, 1885, **47,** 779) examined a sample of camphor oil 5 years old and gives the following as its approximate composition: Lævopinene, 7%; limonene, 20%; camphor, 23%. Yoshida also indicated a new constituent termed by him "camphorogenol," but this has been shown to be non-existent.

The following definite compounds are stated by Schimmel & Co. to exist in camphor oil:

Constituent	Formula	B. p.
Pinene	$C_{10}H_{16}$	158 to 162°
Phellandrene	$C_{10}H_{16}$	170°
Cineol	$C_{10}H_{18}O$	176°
Dipentene	$C_{10}H_{16}$	180°
Camphor	$C_{10}H_{16}O$	206°
Terpineol	$C_{10}H_{18}O$	215 to 218°
Safrol	$C_{10}H_{10}O_2$	232°
Carvacrol	$C_{10}H_{14}O$	236°
Eugenol	$C_{10}H_{12}O_2$	248°
Sesquiterpene	$C_{15}H_{24}$	274°

In the fractions of camphor oil of highest b. p. there occurs an intense blue compound, which is probably identical with the body, boiling at about the same temperature, present in the oils of chamomile, millefolium, wormwood, etc. Caprylic acid is also stated by

Schimmel & Co. to be present in camphor oil, and an acid, belonging probably to the oleic series.

Much of the camphor oil which reaches the market has been deprived of its safrol.

Eight samples of commercial camphor oil obtained in Philadelphia and New York were found by Trimble and Schröter (*Amer. J. Pharm.*, 1889, **61**, 273) to have the following characters:

	Origin of sample	Sp. gr. at 15°	B. p.	Rota-tion	Colour	Odour
1.	Crude Japan oil........	0.9632	180°	+24.5°	Reddish-brown.	Camphor and sassafras.
2.	From Fritzsche Bros.	0.9816	180°	+16.3°	Dark brown.	Camphor and sassafras.
3.	From Fritzsche Bros., "Germany,"	0.8877	170°	+30.5°	Colourless.	Turpentine and camphor.
4.	} Probably the same	0.8863	170°	+31.1°	Same as No. 3	Same as No. 3.
5.	} as No. 3.	0.8803	...	+31.1°	Same as No. 3	Same as No. 3.
6.	New York; "Rectified"	1.006	210°	+14.3°	Light yellow.	Sassafras and slightly camphoraceous.
7.	Philadelphia.........	0.9903	206°	+19.2°	Yellow.	Same as No. 6.
8.	Philadelphia.........	0.9546	198°	+ 0.5°	Dark reddish-brown.	Empyreumatic and camphoraceous.

All the samples had an acid reaction, due to the presence of acetic and formic acids, and were miscible in all proportions with 95% of alcohol.

It is clear that from some of these (*e. g.*, samples 3, 4, and 5) the safrol had been previously separated. They were, further, probably mere fractions of the residual oil, and suitable only for turpentine substitutes. Camphor oils are by-products in the manufacture of camphor and safrol, and should be purchased for what they show on analysis.

Sample No. 1, having been furnished as a typical form of crude Japan oil, was examined more extensively than the others. No aldehyde was found by addition of sodium hydrogen sulphite. The acidity was removed by shaking the sample with water. The neutral oil was boiled for some hours with aqueous solution of alkali. On adding a mineral acid, two layers formed, and from the aqueous layer a distillate containing acetic, formic, and butyric acids was obtained indicating the presence of esters of these acids.

Sujiyama (Schimmel's Report, October, 1902) found 6 samples of light camphor oil to range in sp. gr. from 0.870 to 0.910, and to

yield the following amounts of distillate on fractionation: from 26 to 38% between 175–180°; 30 to 44% between 180–185°; 11 to 19% between 185–190°; 4 to 7% between 190–195°; 2 to 4% between 195–200°; and from 4 to 6% at temperatures exceeding 200°.

Under the title of "*light camphor oil*," Schimmel & Co. have introduced into commerce the lower-boiling fractions of the by-product obtained in the manufacture of safrol. It is stated to have a sp. gr. of 0.895 to 0.900, a flash-point of 44.5,° and a b. p. of 175°. Rectified light camphor oil has been recommended as a substitute for oil of turpentine. Although it cannot adequately replace the latter in the manufacture of paints, light camphor oil is said to be a useful solvent for resins.

Parry has stated that samples of this oil from the London market sometimes have a sp. gr. as low as 0.875 and consist almost entirely of terpenes. This light camphor oil is used to a considerable extent for the adulteration of the more valuable essential oils, such as those of peppermint and eucalyptus.

"*Heavy camphor oil*," as manufactured by Schimmel & Co., is a light green liquid, b. p. 240° to 300°, and having a sp. gr. of 0.960 to 0.970. It is stated to be a good solvent for all sorts of resins, including caoutchouc, and is employed for scenting soft soap, blacking, etc., and for disguising the odour of mineral oil and of fats extracted by carbon disulphide or petroleum spirit. It is viscous, non-poisonous, not readily inflammable, and has marked antiseptic properties. A well-rectified camphor oil, containing much safrol and of sp. gr. 1.050, constitutes the bulk of the so-called American sassafras oil.

For the estimation of *camphor* in camphor oil, H. Löhr (*Chem. Zeit.*, 1901, **25,** 292) proceeds as follows: At least 300 grm. of the oil is fractionated, the distillate below 195°, and those between 195°–220° aand above 220°, being collected separately. The second fraction, which contains the whole of the camphor, is kept in a freezing mixture for 1 hour, when the camphor is filtered off, wrapped in filter-cloth and then in filter-paper, and pressed for 1/2 hour. The cake of camphor thus obtained is wrapped in fresh filter-paper and again pressed for fifteen minutes, and is then weighed. The mother-liquor from which the camphor was previously separated is next redistilled and the fraction at 205° to 220° frozen and treated as before. 5 distillations are necessary to obtain all the camphor from the original fraction containing it.

Caraway Oil.

Caraway oil is obtained by the distillation of the fruit (seed) of *Carum Carvi*. It is a colourless or pale yellow oil, which gradually darkens in colour on keeping. It has a spicy taste.

German "light oil of caraway," also sold under the misleading title "rectified caraway oil," is merely the terpene obtained as a by-product in the manufacture of carvone. It has a sp. gr. of about 0.850 and an opt. rot. exceeding +100°. It is largely employed in soap perfumery.

Oil of caraway consists essentially of dextrolimonene and carvone, $C_{10}H_{14}O$ (see page 212). Possibly a small amount of carvacrol is also present. It is to the carvone that the value of caraway oil is chiefly due. On this account many of the oils of commerce have been partially or wholly deprived of their carvone, which latter commands a high price and is official in certain pharmacopœias. Such inferior oils can be detected by their lowered sp. gr.

Pure carvone has a sp. gr. of 0.963 to 0.966. Commercial "carvone" is often sold having a sp. gr. from 0.933 to 0.944. It is thus merely fractionated caraway oil. Schimmel & Co. have noted the presence of alcohol (about 5%) in such samples of commercial "carvone."

The British Pharmacopœia directs that oil of caraway should have a sp. gr. of 0.910 to 0.920. According to Schimmel and Co., normal oil of caraway may have a sp. gr. of 0.907 (generally, 0.908 to 0.910). J. C. Umney, however, regards 0.910 as being the lowest allowable limit.

According to the investigations of Schimmel & Co., the oil from the young caraway plant is rich in limonene, but poor in carvone. From the riper material, an oil richer in carvone and poor in limonene is obtained. These observations go to show that the terpene is first formed in the plant, and that the oxygenated constituent is subsequently produced from the terpene.

The opt. rot. of oil of caraway is not stated in the British Pharmacopœia (1898), though the United States Pharmacopœia (8th Rev.) gives the limits +70° to +80° at 25°. The rotation of pure oils ranges from about +70° to +85°, the mean of these figures being the average rotation of the oil. The refractive index is given by Parry at 1.4870 to 1.4900.

Caraway oil is soluble in an equal volume of alcohol (90% by volume), and in 3 to 10 volumes of 80% alcohol (United States Pharmacopœia).

A useful method for the valuation of oil of caraway is the fractional distillation of the oil. Genuine oils will show the largest fractions between 170° and 180°' (which contains the whole of the limonene and should not exceed 25%) and 220° and 230° (which contains the carvone and should not be less than 40 to 50%). At least 40% of oil of caraway should distil above 200°.

The presence of a fair amount of carvone in caraway oil may be detected by heating equal parts of the oil and phenyl-hydrazine for a few minutes to 100°, when on cooling the mixture, a mass of light yellow crystals of the *hydrazone*, $C_{10}H_{14}.N.NH.C_6H_5$, will be produced.

J. Henderson (*Pharm. J.*, [4] 1909, **23,** 610) reports a case of adulteration of caraway oil with castor oil. The sp. gr. of the sample corresponded with the requirement of the Br. P. The opt. rot. was +69.7°. The solution with 10 volumes of 80% alcohol was turbid and an estimation of carvone showed 29%. After fractional distillation 16% of castor oil was detected in the residuum.

Cedar-wood Oil.

This oil is obtained from several varieties of cedar, but the oil commonly known under this name, the oil of red cedar-wood, is prepared by the distillation of the wood of *Juniperus virginiana*. The supply comes from many parts of North America, and the oil is often distilled from the waste wood-shavings from the manufacture of lead-pencils. A much inferior oil is sometimes prepared from the condensed vapours of the drying chambers containing the cedar-wood, but the product is devoid of the good odour and other properties of the true cedar-wood oil.

Oil of cedar-wood is a colourless, yellow, or often brownish, thickish oil, with a mild persistent odour. The sp. gr. ranges from about 0.940 or 0.945 to 0.960. It is always lævorotatory, ranging from —25 to —40. It has a high refractive-index (about 1.505 at 17°), and for this reason is much used with connection with oil-immersion lenses. It is soluble in alcohol with difficulty, requiring usually from 10 to 20 parts of 90% alcohol for solution.

When distilled from very old wood, it contains a considerable quan-

tity of *cedrol*, or cedar-camphor. Schimmel & Co. do not consider
that this constituent is an essential one in normal cedar-wood oil, but
that it is formed when the oil is kept under some conditions. Only
small proportions of cedrol are present in cedar-wood oil.

Cedrol, $C_{15}H_{26}O$, was obtained from cedar-wood 'oil, in 1841, by
Walter (*Ann.*, 1841, **39,** 247). It forms, when pure, silky crystals
with a pleasant aromatic odour. It melts at 78° to 80°.

Besides cedar-camphor, there are present in this oil the sesquiterpene
cedrene (see page 186), and possibly also cadinene.

Good samples of cedar-wood oil should not contain more than about
10% of the crystalline cedrol (cedar-camphor). Parry obtained, by
the examination of 4 genuine samples. 2.32, 2.21, 2.13, and 1.72%
of potassium hydroxide required for the saponification of the acetylated
oils. The results are somewhat low, owing to the dehydrating action
of the acetic anhydride used in the acetylation.

Cedar-wood oil is largely used as an adulterant of sandalwood oil.
It may be detected and estimated as described on page 392. In
addition to its employment with oil-immersion lenses, it is used in
soap perfumery.

Adulteration of this oil is not very frequent. Pure oil may be known
by its sp. gr., high lævorotatory power, and the saponification values
before and after acetylation.

The following table gives the chief characters of the less impor-
tant oils of commerce (chiefly from Schimmel's reports). Oil of
Jamaica or Honduras cedar is in reality not a cedar oil, and is more
correctly termed "cedrela oil." It is, however, conveniently included
in this table. Many others of these oils are most probably obtained
from the wood of *Cedrela* species:

Oil	Source	Sp. gr.	Opt. rot.	Characters and constituents
Cedar-wood, Lebanon......	Wood of *Cedrus libani.*	0.985	− 10.8°	Brownish-yellow oil of pleasant odour.
Cedar-wood, Corinto.......	Unknown.	0.906	− 17.3°	Yellow oil.
Cedar-wood, Cuba.........	Unknown.	0.923	+ 18.1°	Yellowish oil, containing cadinene.
Cedar-wood, La Plata....	Unknown.	0.928	Inactive.	Bright blue.
Cedar-wood, Costa Rica .	Unknown.	0.915	− 5.9°	Yellow oil, consisting chiefly of cadinene.
Cedrela (Jamaica cedar-wood)	*Cedrela odorata*	0.935	About − 1°	
Cedar-wood, Hayti	Unknown.	0.961	− 15°	High in alcohols.
Cedar-wood	*Cedrus atlantica*	0.951	+ 60°	Contains libanone, a ketone: also dextro-cadinene.

Cedar-leaf Oil.

This oil should, presumably, be obtained by the distillation of the leaves of the red cedar, *Juniperus virginiana*, but other leaves, such as of *Thuja occidentalis*, are used in its preparation. Many conifers in North America pass under the name of "cedar"; thus *Thuja occidentalis*, and *Chamæcyparis sphæroidea* are termed "white cedar."

The true cedar-leaf oil, from *J. virginiana*, is rarely found on the market. It is an oil having a pleasant, sweetish odour. Gildemeister and Hoffmann (*The Volatile Oils*) state that this oil has a sp. gr. of 0.887, and an opt. rot. of +54.9°. It is insoluble in 16 parts of 80% alcohol. A large portion of the oil distils below 180°, of which the greater part comes over between 173° and 176°. This fraction consists of dextrolimonene. Other terpenes are also present, including, probably, pinene. Cadinene is contained in the higher fractions, while borneol and bornyl esters (including probably bornyl valerate) are also present in the oil.

The following analyses of commercial oils show the differences existing between them and pure oil of cedar-leaf are given by Schimmel & Co. (*Rep.* April, 1898, 14):

Sp. gr.	Opt. rot.	Sol. in 70% alcohol
0.897	−12.4°	Insoluble
0.886	− 3.7°	Insoluble
0.887	−24.2°	Insoluble
0.920	−10.4°	1 in 4
0.918	−11°	1 in 5
0.905	−10°	Insoluble

All these samples contained more or less oil of thuja, as was evident from their odour.

Commercial oil of cedar-leaf is thus usually obtained by the distillation of miscellaneous conifer-needles, including those of thuja. Red thuja oil is sometimes met with under the name "cedar oil." The true cedar-leaf oil is much more valuable than either cedar-wood oil or the oils from thuja and other varieties of conifers.

Celery Oil.

Schimmel & Co (*Rep.*, 1909, 37) give the following data for an oil distilled from a wild celery in the south of France. It was pale

yellow and of a pronounced celery odor. No clear solution could
be obtained even with 95% alcohol, due to the fact that the sample
was about a year old and had become much resinified. By distilla-
tion with steam (leaving 7.7% residuum) the constants were: sp. gr.
15° 0.8541; opt. act., 70° 55'; ind. ref. 1.47489. This rectified
sample was soluble in 6 volumes and more of 90% alcohol.

Chamomile Oils.

Chamomile oil occurs in commerce in 2 varieties, namely, Roman
chamomile oil and German chamomile oil. The former is the oil
distilled from the flowers of *Anthemis nobilis;* the latter is obtained
from the flowers of *Matricaria chamomilla.*

Roman chamomile oil is official in the British Pharmacopœia
(1898), which describes it as a pale blue or greenish-blue oil when
freshly distilled, gradually becoming yellowish-brown. It has the
aromatic taste and odour of the flowers. The sp. gr. of the oil ranges
from 0.904 to 0.916 at 15°, and it is only slightly optically active
($+1°$ to $+4°$).

Roman chamomile oil is remarkable for the number of compounds
of the aliphatic series which occur in it. These compounds include
isobutyl isobutyrate and angelate; amyl tiglate and angelate; hexyl
tiglate and angelate; and *anthemol,* $C_{10}H_{16}O$, as was shown by the
researches of Demarcay. Naudin (*Bull. Soc. Chim.* [2], 1884, **41,** 483)
also isolated a hydrocarbon of the olefine series, which contained
$C_{18}H_{36}$ and was termed by him *anthemene.* It crystallises in needles,
m. p. 63°.

According to Blaise (*Bull. Soc. Chim.* [3], 1903, **29,** 327), Roman
chamomile oil does not contain any compound of tiglic acid, the small
quantities usually found being due to the action of alkali on the angelic
acid on saponification. Angelic acid forms 80% of the total acids
in the oil.

Angelic and *tiglic acids* are stereo-isomers, unsaturated acids of the
acrylic series.

Angelic acid melts at 45°, while tiglic acid melts at 64.5° to 65°.

There are no recognised methods for the analysis of chamomile
oil. The properties, as described by the Pharmacopœia, should be
noted. This is characteristic, both in the case of Roman and German
chamomile oils. Doubtful samples should be submitted to a compara-

tive test with a specimen of the pure oil. The sp. gr. of the Roman chamomile oil should come within the limits specified above.

A. Jama (*Apoth. Ztg.*, 1909, **24**, 585) obtained oils from both calyx and the entire flower and found the following data:

Flower, sp. gr. 0.954., ind. ref. 1.3637, sup. no. 74.4;

Calyx, sp. gr. 0.949, ind. ref. 1.3637, sup. no. 33.7.

Neither oil had appreciable optical activity.

Chrysanthemum oil, distilled from the green leaves of *Chrysan-themum caponicum* (the autumn chrysanthemum), is considered by Perrier to resemble the oil of Roman chamomile. The yield is about 0.16% of a green oil having an odour of peppermint and chamomile. Chrysanthemum oil begins to boil at 160°, and has a sp. gr. of 0.932 at 15° and a ref. index of 1.4931 at 18°. It is soluble in 10 volumes of 95% alcohol, but nearly insoluble in alcohol of 70%. When cooled to a very low temperature, the oil solidifies. It contains an aldehydic substance which combines with sodium hydrogen sulphite, and it apparently also contains angelic acid.

German chamomile oil is blue, the colour changing gradually by the influence of light to green, and finally brown. Its sp. gr. at 15° is 0.930 to 0.945. It was found by Kachler to contain an acid which has since been identified as *caprinic acid*. Schimmel & Co. state that the average saponification-number is 45; it is highly probable that it contains a notable quantity of esters.

German chamomile oil, when cooled to a low temperature, becomes a semi-solid mass of the consistency of butter. Schimmel & Co. (*Report*, April, 1894) have shown that this behaviour is due to the presence of a paraffin or mixture of hydrocarbons. This buttery substance dissolves with difficulty in alcohol; but it is readily soluble in ether, and persistently retains the blue of the oil. When quite pure, it is said to be a brilliant white body, m. p. 53° to 54°, showing all the properties of a paraffin.

German chamomile oil of commerce is said to be sometimes adulter-ated with oil of milfoil and with cedar-wood oil. Oil of milfoil is a blue oil, but as its odour is quite different from that of chamomile oil, it would be impossible to add it in any quantity without detection. Chamomile oil adulterated with an appreciable quantity of cedar-wood oil remains liquid at 0° (Schimmel & Co.), whereas the genuine oil begins to thicken at 15° and congeals at 1°. The oils of copaiba, lemon, and turpentine are also used as adulterants of chamomile oil.

Clove Oil.

Clove oil is obtained by distillation from the buds and stems of *Eugenia caryophyllata*. A cheap and inferior oil is made from the *stalks* of the clove-plant. It appears to contain no acetyl-eugenol.

Clove oil has the characteristic odour of cloves, and a pungent taste. When freshly distilled the oil is colourless or faintly yellow, but the colour deepens on keeping. Clove oil is soluble in about 60 pts. of proof spirit, and dissolves in rectified spirit and glacial acetic acid in all proportions. The oil is also soluble in about 2 vols. of 70% alcohol. The sp. gr. varies from not less than 1.050 to 1.068. Any sample with a lower sp. gr. than 1.050 is adulterated or suspicious. The opt. rot. of clove oil ranges from 0 to −1, and the b. p. should not be below 245°. The ref. index of the oil is an additional guide to its purity, the index of eugenol itself being 1.5412 at 20° (W. H. Simmons).

E. J. Parry states that a sample of clove oil examined by him, which was an absolutely pure oil guaranteed by one of the most reputable drawers in England, had the low sp. gr. 1.0494 at 15.5°. It contained 84% of eugenol estimated by Umney's potassium hydroxide absorption method, and answered to the British Pharmacopœia tests in all other particulars. Parry suggests 1.048 as the minimum limit for the sp. gr. of the oil. Schimmel & Co. consider the limits of 1.045 to 1.070 to be compatible with genuine oils.

The chief and most important and abundant constituent of clove oil is the phenoloid substance, eugenol, $C_{10}H_{12}O_2$, the proportion ranging from 80 to 95%. The greater part of the eugenol is free, but there exist in clove oil esters of eugenol (chiefly acetate) in amount ranging from 7 to 17%. The sesquiterpene, caryophyllene, makes up the greater part of the remaining portion of the oil. Jorissen states that oil of cloves contains traces of a substance resembling or identical with vanillin, which possibly has its origin in the oxidation of eugenol. Heine & Co. state that traces of naphthalene are present in clove oil. Schimmel & Co. have found methyl-alcohol, furfurol, and traces of an aldehyde (not acetaldehyde). They consider that the darkening of oil of cloves is probably partly due to the presence of furfurol.

Schimmel & Co. (*Rep.*, April, 1897, 45) have isolated from clove oil a very small quantity of a substance which appears to be normal amyl-methyl-ketone, $C_5H_{11}.CO.CH_3$. This is believed by them to be the other odoriferous constituent of the oil, as it imparts to a mixture of

eugenol and caryophyllene a clove-like odour, even when added only in traces. More recently, the discovery of methyl-heptyl-ketone and methyl benzoate in clove oil has been announced by Schimmel & Co. (*Rep.*, 1902 and 1903, April).

Erdmann has observed the presence in clove oil of salicylic acid, probably combined as eugenol acetyl-salicylate. The same worker also confirmed Schimmel & Co.'s observations of the presence of furfurol in the preliminary distillate of cloves.

The British Pharmacopœia (1898) states that oil of cloves should have a sp. gr. of not less than 1.050, and that the alcoholic solution should turn blue with ferric chloride. When shaken with 1 vol. of ammonia, clove oil should form a semi-solid yellowish mass due to the presence of eugenol.

Unless the proportion of ferric chloride is very small, a bright green is produced. After shaking 1 pt. of the oil with 20 pts. of *hot* water, and filtering the aqueous liquid, the latter should not give a blue with ferric chloride (absence of phenol), though a transient grey-green may be produced (United States Pharmacopœia).

Alcohol is occasionally added as an adulterant to oil of cloves. It lowers the characteristically high sp. gr. of the oil, and begins to distil over below 100°, whereas pure clove oil will yield no distillate below 245°.

Petroleum and oil of turpentine are sometimes used as adulterants of oil of cloves. Such sophistications can readily be detected by the decreased solubility of the oil in 90% alcohol.

The cheaper kinds of German clove oil are liable to partial abstraction of eugenol, or may be a mixture of pure oil with the residue (caryophyllene) from the manufacture of eugenol. Such oils have a low sp. gr., and are less soluble in 90% alcohol than pure oil of cloves. The eugenol content will be lessened.

An oil which was said to be used in certain German works as an adulterant of clove oil was found by Parry to consist of pure cedar-wood oil. Such an adulterant would lower the sp. gr. of the oil, whilst it would render it less soluble in 90% alcohol. It would also increase the lævorotation.

The various methods for the estimation of eugenol in clove and other oils are described on page 294. According to E. C. Spurge (*Pharm. J.* [4], 1903, **16**, 701, 757), the estimation of the eugenol by Umney's method (uncorrected), together with the observation of the

sp. gr., is sufficient for a pharmacopœia test. The United States Pharmacopœia requires clove oil to contain at least 80% of eugenol when assayed by Umney's method (p. 294), 10 c.c. of the oil being employed with 100 c.c. of 5% potassium hydroxide solution, with which latter solution also the liquid is brought to the zero-mark in the flask.

Coriander Oil.

Coriander oil is distilled from the fruit of *Coriandrum sativum*. It is a colourless or pale yellow oil, having an odour and flavour of the fruit.

The British Pharmacopœia (1898) directs that the oil should have a sp. gr. of 0.870 to 0.885, and that 1 c.c. of the oil should yield a clear solution with 3 c.c. of 70% alcohol. The latter test shows the absence of oil of turpentine and added terpenes.

The constituents of coriander oil have not been very thoroughly studied. Pinene is undoubtedly present. The alcohol found by Semmler, and termed by him "coriandrol," has been proved by Barbier (*Compt. rend.*, 1893, **116**, 1459) to be dextrolinalol, $C_{10}H_{18}O$. This is the chief constituent. The substance to which oil of coriander owes its characteristic odour has not yet been isolated.

Oil of coriander differs in its composition according as it has been obtained from ripe or unripe fruits. The oil from the ripe fruit answers to the British Pharmacopœia limits. Schimmel & Co. have investigated the nature of the oils distilled from the fruit, etc., at various periods of its growth. The results are shown in the following table:

Nature of material	Sp. gr. at 15.5°	Rotation	Solubility in 70% alcohol	Remarks
1. Oil from the entire flowering plant (green).	0.853	. . . .	Insoluble	Objectionable odour which had almost entirely disappeared after 2 1/2 months.
Same, after keeping 2 1/2 months.	0.856	+ 1.03°	. . . .	. . . .
2. From green half-ripe herb with fruits.	0.866	+ 7.2°	1 : 3	Odour of coriander with slight objectionable odour.
Same, after keeping 1 month.	0.869	. . . .	. . . .	Pure coriander odour.
3. From ripe coriander fruit.	0.876	+ 10.8°	1 : 3	. . . .

Schimmel & Co. (Rep., Oct., 1909, 47) found ind. ref. 1.4638 and ester number 20.22 in a sample distilled from ripe coriander seed.

Schimmel & Co. consider that the linalool content should be 60 to 70%.

Parry (*Chemistry of Essential Oils*, 2d ed.) gives the sp. gr. of pure coriander oil as 0.870 to 0.880, the optical rotation as +8° to +14°, rarely falling to +7°, and the ref. index as 1.4650.

The opt. rot. of oil of coriander is not stated in the British Pharmacopœia. It ranges from +6° to +15° (United States Pharmacopœia, +7° to +14°).

The chief constituent of the oil being linalol, a large fraction (about 45 to 50%) should distil at 190° to 200°.

Orange oil, turpentine oil, and the oils of cedar-wood and cubeb have been used as adulterants of coriander oil. Orange and turpentine oils will be detected by the increase in the opt. rot., and also by the lowering of the sp. gr. The reverse effects will be produced by cedar and cubeb oils.

Cubeb Oil.

This oil is obtained by the distillation of the unripe dried fruit of *Piper cubeba*. It is usually greenish or greenish-blue (occasionally greenish-yellow), and has the characteristic odour and flavour of cubebs.

The British Pharmacopœia (1898) states that the sp. gr. of the oil ranges from 0.910 to 0.930, but most samples of genuine oil of cubebs have a sp. gr. of 0.920 to 0.930. The rotation (not stated in British Pharmacopœia) ranges between —25 and —40° (average about —30°), the lower limit being that given by Gildemeister and Hoffmann (*The Volatile Oils*), and adopted in the United States Pharmacopœia (8th Rev.), which gives —25° to —40°.

The constituents of this oil have not as yet been thoroughly determined. 1 or more terpenes (including dipentene and probably pinene or camphene), and 2 sesquiterpenes (including cadinene) exist in the oil. Besides these, a sesquiterpene alcohol of the formula $C_{15}H_{25}OH$ is present, especially in the case of oils distilled from old oxidised fruits. This substance is the so-called "*cubeb-camphor.*" It crystallises in rhombic prisms melting at 65° to 67° (or, according to Winckler, at 70°) and boils at 245° to 248° with partial decomposition.

The oil begins to boil at about 175° and distils mainly between 250° and 270°. A genuine oil on fractional distillation gave the follow-

ing results: Below 250, 9%; 250° to 260°, 27; 260° to 270°, 48; 270° to 280°, 7; above 280°, 9%.

The higher fractions of the oil are blue, which has been erroneously ascribed to the presence of copper. The cause is unknown.

Oil of cubebs is now rarely adulterated, owing to its low price. The presence of turpentine oil would be revealed on fractionation. Genuine oil of cubebs is soluble in 1 to 2.5 pts. of 90% alcohol.

Cumin Oil or Cummin Oil. (Roman Caraway Oil.)

This oil is obtained by the distillation of the fruit from *Cuminum cyminum*. It is an almost colourless or light yellow oil, with a characteristic odour and bitterness.

The oil from the fruit obtained in the Levant has a sp. gr. of 0.910 to 0.930; Indian oil has a slightly lower sp. gr., 0.893 to 0.899. The opt. rot. of these oils ranges from +4 to +8.

Oil of cumin is fairly soluble in 80% alcohol. The solubility of the oil depends upon the amount of cumic aldehyde present, oils of a high sp. gr. (containing much of this heavy constituent), being soluble in 3 parts of 80% alcohol, and lighter oils repuiring as much as 10 parts of 80% alcohol.

The oil contains a terpene which has not yet been identified; cymene; and cumic aldehyde ("cuminol"), $C_{10}H_{12}O$. The last-named constituent may be isolated and estimated in the following way (Kraut, *Ann.*, 1854, **92**, 66):   The terpenes of the oil are removed by distillation, only the portion boiling above 190° being reserved for further treatment.   This high-boiling fraction is next shaken with sodium hydrogen sulphite solution, the resultant crystalline mass being pressed after standing for 24 hours.   The crystals are then washed with a mixture of alcohol and ether, and distilled with a solution of sodium carbonate.

Wolpian (*Pharm. Zeit. Russ.*, 1896, **35**, 97) isolated this terpene which he found to have a b. p. of 157° to 158°, sp. gr. 0.8604, and a rotation of +25.4. To this he gave the name "hydrocuminene." But the evidence is not sufficient to show this substance to be a distinct and hitherto unknown chemical individual.

It has been pointed out by Gildemeister and Hoffmann that if cumic aldehyde is a true aldehyde, the name "cuminol" is incorrect, and should be "cuminal."

Dill Oil.

This oil is distilled from the fruit of *Peucedanum (Anethum) grave-olens*. It is pale yellow, with an odour of the fruit and a sweet, aromatic taste. The British Pharmacopœia (1898) requires it to have a sp. gr. of 0.905 to 0.920 at 15.5°. It should have an opt. rot. of not less than +70.

The constituents of the oil of dill comprise carvone, dextrolimonene, phellandrene (stated by Schimmel & Co. to be present in English and Spanish oils), a paraffin-hydrocarbon, and "dill-apiol" (in Indian dill oil, which is the product of *Anethum Sowa*). This substance is isomeric with "apiol," present in oil of parsley.

Oil of dill thus resembles caraway oil in composition, but it contains less carvone than the latter oil. The odours of the 2 oils are quite different.

Oil of dill differs in character according to its origin. J. C. Umney (*Pharm. J.* [4], 1898, **7**, 176) has pointed out the differences between the oil obtained from English fruits and that from India dill fruit. Indian oil of dill has a higher sp. gr. and a smaller carvone content than the English oil. The following results were obtained by Umney on 5 samples of oil of dill. The Japanese oil resembles Indian dill oil in its characters:

Oil	Sp. gr.	Rotation	Fractional distillation, %				
			Below 200°	200–210°	210–220°	220–230°	Above 230°
English.......	0.9148	+72.25°	22	14	12	50	2
English.......	0.9146	+80.25°	21	19	12	46	2
German.......	0.9002	+70.25°	53	13	12	17	5
Indian........	0.9486	+47.5°	24	17.5	7	10.5	39
Japanese......	0.9643	+50.5°	21	12	10	8	49

German dill oil is similar to English dill oil, but Umney considers that the above sample of German dill oil has suffered partial depriva-tion of its carvone. E. J. Parry (*Chemistry of Essential Oils*) concurs with Umney's statement as to the probable abstraction of carvone from dill oil having a sp. gr. below 0.905 at 15.5°. Schimmel & Co. state that although the sp. gr. of this sample is somewhat low, yet it is quite consistent with a pure oil. They record 8 examples of oils of Thuringian dill with sp. gr. ranging from 0.899 to 0.911.

The physical constants of dill oil are the most trustworthy by which to judge of the quality of a sample. The sp. gr. should lie between 0.910 and 0.925, and the opt. rot. should be from +70 to +80. These figures should be taken as maximum and minimum limits. Fractional distillation is valuable as a method for the approximate estimation of carvone. Not more than 15 to 20% of the oil should distil below 185°, and at least 35 to 40% between 185° and 225°. Parry states that not less than 40% should distil above 220°. The ref. index is about 1.4900.

In order to exclude the apiol-containing oil from Asiatic fruits, the official characters of the oil (*Oleum Anethi*) should be adhered to (Umney).

Dill-apiol, like its isomer apiol, is converted by the action of alcoholic potassium hydroxide into an isomeric product, by an alteration of the allyl- to the propenyl-group. Dill-apiol is a thick, oily liquid, with a b. p. of 285°. Iso-dill-apiol, formed by the action of alcoholic potassium hydroxide, is a substance forming colourless prisms melting at 44°, and boiling with slight decomposition at 296°. Bromine forms a tribromoderivative with both apiol and dill-apiol.

Eucalyptus Oils.

The oils distilled from the leaves of species of *Eucalyptus* differ so much in their physical characters and chemical composition that no sufficient indication is afforded of the nature of the oil unless the species of eucalyptus is stated.

The constituents of these oils include dextro- and lævopinenes (the former of which was at first termed "eucalyptene"); phellandrene; probably camphene and fenchene; the sesquiterpene aromadendrene; cineol (eucalyptol); citronellal; citral; cuminal (?); citronellol; geraniol; geranyl acetate, and various aldehydes and esters; and the stearoptene eudesmol (p. 341). The oils used in medicine contain cineol as chief constituent. The official oil of the British Pharmacopœia (1898) is that from *E. globulus*, which usually contains at least 50 to 60% of cineol, and frequently up to 80%, together with pinene and traces of ethyl alcohol, amyl alcohol, and butyric, caproic, and valeric aldehydes.

According to H. G. Smith, the aldehyde occurring in a large number of eucalyptus oils is not cumic aldehyde, as hitherto supposed, but a new aldehyde to which he gives the name aromadendral (p. 341).

The official oil (from *E. globulus*) is the most valued in medicine. The oils from *E. cneorifolia*, *E. dumosa*, *E. leucoxylon*, *E. oleosa*, *E. punctata* and *E. Morrisii* resemble that from *E. globulus* very closely in physical characters and chemical composition, and therefore frequently comply with the requirements of the British Pharmacopœia. An oil answering to these requirements is colourless or pale yellow, having an aromatic camphoraceous odour and a pungent taste, leaving a sensation of coldness in the mouth. Sp. gr. 0.910 to 0.930. It should not rotate the plane of a ray of polarised light more than 10° in either direction, and it should become semi-solid on being stirred, when cold, with a third or half its volume of phosphoric acid of commerce of sp. gr. 1.750 (presence of a due proportion of cineol). If to 1 c.c. of the oil there are added 2 c.c. of glacial acetic acid and 2 c.c. of a saturated aqueous solution of sodium nitrite, the mixture, when gently stirred, should not form a crystalline mass (exclusion of eucalyptus oils containing much phellandrene). This last-named test is included in the United States Pharmacopœia (8th Rev.).

The sp. gr. of the oils of eucalyptus range from 0.850 to 0.930 at 15°. The lower figure is only reached in the case of the oil from the leaves of *E. amygdalina*, which is largely composed of phellandrene, with very little cineol. The other oils range in sp. gr. from 0.870 to 0.930. Oils rich in phellandrene have a low sp. gr., whilst those having a high cineol-content approach the higher limit, 0.930, which is the sp. gr. of pure cineol.

It has been pointed out by W. J. Brownscombe that eucalyptus oils other than *E. globulus* often answer the British Pharmacopœia tests, whilst some globulus oils do not respond to all the official requirements. Amongst the oils which have a fairly high cineol content, and yet do not exactly conform to the tests of the Pharmacopœia, are those from *E. eugenoides*, *E. macrorrhyncha*, and *E. odorata*. The last-named contains a notable amount of phellandrene.

Some authorities have suggested that the minimum sp. gr. of the British Pharmacopœia oil might preferably be fixed at 0.905. Oils having a cineol content of 45 to 52% and answering to the pharmacopœial requirements in every other respect, have been found to have sp. gr. ranging from 0.906 to 0.910 at 15°. Allen examined pure samples ranging from 0.907 to 0.930. The British Pharmacopœia limits are preferable, as they tend to keep up the cineol content.

It is not to be assumed, however, that any eucalyptus oil of sp. gr. near 0.930 is necessarily composed mainly of cineol. The researches of Baker and Smith (*J. & Proc. Roy Soc., N. S. Wales*, 1898, **32,** 104, 195) have shown that eudesmol and other high-boiling constituents of the oil of certain species of eucalyptus have high sp. gr. Thus an oil containing a large proportion of eudesmol and a small amount of cineol will have a high sp. gr.

The rotation of the oils of eucalyptus is as irregular as the sp. gr. This is only to be expected, since some oils contain much of the inactive cineol, while others consist mainly of phellandrene, which has a very high optical rotation. The official oil is limited in its optical rotation from $+10$ to -10. Oils between these limits of optical activity and of the correct sp. gr. will contain a proper percentage of cineol. The optical rotation is not of much value. The U. S. Pharmacopœia requires eucalyptus oil to be dextrorotatory, up to $+10°$.

A pure sample of globulus oil examined by the author showed a ref. index of 1.4642 at $25°$. The ref. index of pure cineol is said to be 1.4596 at $17°$.

The most convenient test for the presence of phellandrene is based on the formation of *phellandrene nitrite*, $C_{10}H_{16}N_2O_3$. If much phellandrene is present, a crystalline mass of this compound will be produced when the oil is mixed with glacial acetic acid and sodium nitrite solution. A sample of eucalyptus oil purchased under the Sale of Food and Drugs Acts, and examined by A. R. Tankard in Allen's laboratory, had a sp. gr. of 0.8897, contained little or no cineol, but much phellandrene. It had a ref. index of 1.4830 at $25°$.

It has been shown by H. G. Smith (*Chemist and Druggist*, 1899, **54,** 534) that some eucalyptus oils are dextrorotatory when they contain the maximum amount of cineol, and that they do not then contain phellandrene, though this constituent may be present at certain times of the year.

According to Baker and Smith (*Chemist and Druggist*, 1899, **54,** 299) the emerald-green given by eucalyptus oils with the pharmaco-pœial nitrite test is not due to phellandrene, but to the pinenes present. Oils in which dextropinene is predominant are stated to give the colour to a more marked degree than those which contain an excess of lævopinene. Turpentine oil gives a brilliant green. A pure sample of *E. globulus* examined by Baker and Smith gave only a dull green with the nitrite test. The oil from *E. microcorys*, which consists very largely

of dextropinene with some cineol, but contains no phellandrene, is
stated by Baker and Smith to give a marked green. It is worthy of
notice that an oil containing no cineol may give a more pronounced
green than a pure oil.

Estimation of Cineol.—The phellandrene test and the estimation
of the percentage of cineol are the most useful data on which to judge
the quality of oils of eucalyptus. The British Pharmacopœia test for
the presence of a due content of cineol is much too indefinite, but the
United States Pharmacopœia method of assay is sufficiently accurate
for most purposes (see p. 340). Several methods of estimating cineol
have been based on reaction with phosphoric acid. It was first
pointed out by Scammel (Brit. patent, 1894, 14138) that by the addi-
tion of concentrated phosphoric acid (sp. gr. 1.75 to 1.785, preferably
the latter) in slight excess to the cineol-containing oil at a temperature
not exceeding 60° F., the whole of the cineol is thrown down in the
form of the crystalline phosphate. The cineol phosphate may then
be treated in several ways. Thus it may be thoroughly pressed be-
tween blotting-paper, and the cake of phosphate weighed; or it may
be decomposed with water (cold), and the free cineol weighed (as
recommended by Scammel, who, however, used *hot* water); or the so-
lution of cineol phosphate in water may be titrated, and the cineol
calculated from the phosphoric acid indicated, assuming that one
molecule of phosphoric acid is equivalent to one molecule of cineol.

E. J. Parry (*Chemistry of Essential Oils*) states that in his opinion this
process, when carefully worked, gives results accurate to 3% when the
oil contains at least 30% of cineol. If the cineol content is lower than
this, the oil must be previously fractionated. Faulding (*Chemist and
Druggist*, 1895, **46**, 311) also states that the cineol is quantitatively
separated by Scammel's process.

According to H. G. Smith (*Chem. News*, 1902, **85**, 3), the pink
obtained with some eucalyptus oils in the phosphoric acid test is due
to a sesquiterpene termed by him *aromadendrene*. This hydrocarbon
occurs in large amounts in the oil from *E. hæmastoma*. Aromaden-
drene boils at 260° to 265°, and has a sp. gr. of 0.925 at 19°. When the
vapour of bromine is allowed to fall on its solution in glacial acetic acid,
aromadendrene gives a crimson colour, which quickly changes to
violet and finally to a deep indigo-blue.

With regard to the weighing of the pressed cake of cineol phosphate,
D. B. Dott (*Pharm. J.* [4], 1899, **8**, 57) states that in order to ensure the

absence of terpenes and uncombined acid from the phosphate, it is essential to press the mass repeatedly between folds of blotting-paper. This requires some time, and there is risk of the absorption of water by the hygroscopic compound, thus causing error. The second method of procedure, that of weighing the free cineol after the decomposition of the phosphate compound with cold water, is held by Dott to be liable to give a result in excess of the truth, since the free cineol often contains a considerable quantity of undecomposed phosphate in solution. On the other hand, if *hot water* or sodium carbonate solution be used to decompose the phosphate, loss may result owing to solution of the free cineol.

Dott has pointed out that cineol is much more soluble in diluted phosphoric acid than in water.

The third method, namely, that of titrating the phosphoric acid combined with the cineol, is preferred by Dott to the weighing of the pressed compound or of the free cineol. Too great an excess of phosphoric acid must be avoided. This is best done by determining approximately the amount of cineol present, and then making another determination with only a slight excess of phosphoric acid. L. F. Kebler recommends the following procedure (*Amer. J. Pharm.*, 1898, **70,** 492): 8 grm. (or less) of the oil in a beaker is cooled in ice-water, 4 c.c. of phosphoric acid solution (sp. gr. 1.75) added, and the mixture again placed in ice-water. When cool, the contents of the beaker are slowly and thoroughly mixed with a glass rod, the cineol phosphate separated, pressed, weighed, and decomposed with hot water. The acid is then titrated with a standard potassium hydroxide solution. According to the cineol content of the oil, it is occasionally necessary to add more than the specified quantity of phosphoric acid. Kebler obtained, by working on pure cineol, a result showing 103.75%. Fair approximations to the truth are thus obtained, the process being easy and rapid. Dott thinks it probable that as water decomposes the phosphate compound, better results would be obtainable if anhydrous phosphoric acid were used.

W. H. Allen (*Chem. and Drug.*, 1899, **54,** 641) employs *warm* water for the decomposition of the phosphate compound, and finally washes the liberated cineol with warm water to remove any adhering traces of phosphoric acid.

This process with slight modification has been adopted in the United States Pharmacopœia (8th Rev.): 10 c.c. of the oil (eucalyptus,

cajuput) is dissolved in 50 c.c. of "purified petroleum" (petroleum-ether, b. p. 45° to 60°) and phosphoric acid added to the ice-cold liquid drop by drop with constant stirring until the cineol phosphate assumes a yellow or pinkish colour. The precipitate is filtered by means of the pump and washed with cold petroleum-ether. The pressed cake of phosphate is decomposed with *warm* water and the cineol measured. The United States Pharmacopœia requires eucalyptus oil to contain not less than 50% of cineol.

The following process was described by Schimmel & Co. in the *Report*, 1909, **48**, 100 c.c. of the oil containing cineol are mixed in a cassia flask of 100 c.c. capacity with so much 50% resorcinol solution that the flask is filled for about 4/5. The mixture is shaken thoroughly for 5 minutes, and the oil portions which have not entered into reaction are brought into the neck of the flask by adding resorcinol solution, and their volume determined. By subtracting this volume from 10 the cineol content of the oil is obtained, which is then expressed in % by volume by multiplication with 10.

Eucalyptus oil has suffered adulteration by abstraction of its active constituent, cineol, and C. T. Bennett has recorded an instance of the wholesale sophistication of eucalyptus oil with 20% of castor oil. (*Chemist and Drug.*, 1905, **67**, 33). The samples had a somewhat low cineol content, and left a considerable amount of viscous residue on distillation. This residue required a large proportion of potassium hydroxide for saponification, and glycerol was present in the liquid. Castor oil was detected by the usual tests. The presence of this adulterant is likely to be overlooked unless special tests are applied.

The researches of Baker and Smith (*J. & Proc. Roy. Soc.*, N. S. Wales, 1898, **32**, 104, 195; 1900, **34**, 72, 136, 142, 286) have revealed the presence of several new compounds in eucalyptus oils. These observers investigated the oils obtained from the eucalyptus plants of Australia with the result that many are now known to be quite free from cineol, and to contain large quantities of hitherto unrecognised constituents. The new compounds have all been obtained from the high-boiling fractions, and have a high sp. gr. Among them are: 1. Eudesmol, $C_{10}H_{18}O$, a camphor or stearoptene; 2. the amyl ester of eudesmic acid (solid); 3. geranyl acetate, occurring in the oil of *E. Macarthuri* to the extent of 60 to 75%; 4. aromadendral, $C_{10}H_{14}O$, the aldehyde previously supposed to be cumic aldehyde (although this latter does occur in some oils); 5. esters, such as those

of valeric and acetic acids; and 6. piperitone, a ketone of peppermint odour, occurring in the oils of *E. rossi*, *E. Risdoni*, and *E. piperita*.

Eudesmol is isomeric with ordinary camphor, and has been found in the oils from *E. capitellata*, *macrorrhyncha*, *Smithii*, *piperita*, *goniocalyx*, *camphora*, the last-named oil containing a large amount of this constituent. It is a white solid crystallising in milky needles, melting about 80° and boiling at 271°. Eudesmol yields a dinitro compound (m. p., 90°) and a dibromide (56°), but does not form a nitrosochloride. On oxidation with dilute nitric acid, eudesmol is converted into camphoronic acid, but no camphoric acid is formed.

The oil from *E. Macarthuri*, containing 60% of geranyl acetate and 10% of geraniol, together with some eudesmol, but no phellandrene or cineol, differs entirely in appearance and odour from ordinary commercial oil of eucalyptus. It is always slightly dextrorotatory. The geranyl acetate present in the oil is completely saponified in the cold by alcoholic potassium hydroxide in 90 minutes, which fact, as pointed out by H. G. Smith, might be utilised in the determination of this constituent in essential oils in the presence of other esters.

The amyl ester of eudesmic acid, $C_{14}H_{18}O_2$, is present in the oil from *E. aggregata* to the extent of about 57%, and is apparently a homologue of cinnamic acid. Eudesmic acid is only slightly soluble in cold, but readily soluble in hot water. It forms a dibromide.

H. G. Smith has shown that cineol and eudesmol are nearly allied to one another, since the latter may be converted into cineol by keeping the crude fraction for some time in the presence of oxygen, under suitable conditions. Smith suggests that eudesmol is present at certain times of the year in all oils which are eventually rich in cineol.

The following list comprises the greater number of the best-known eucalyptus oils. Further information will be found in E. J. Parry's *Chemistry of Essential Oils*, Gildemeister and Hoffmann's *The Volatile Oils*, and in Schimmel & Co.'s *Reports* (see especially *Report* for October, 1904).

Botanical origin	Yield, %	Sp. gr. at 15°	Opt. rot.	Chief constituents
Eucalyptus amygdalina.	To 3.5	0.850 to 0.886	−25° to −70°	Phellandrene; cineol.
E. Baileyana.	1.0	0.890 to 0.940	. . . .	Cineol; citral; phellandrene.
E. cneorifolia.	. . . .	0.899 to 0.923	−4° to −14°	Cineol; cuminal.
E. dealbata.	3	0.871 to 0.900	. . . .	Citronellal; citronellol
E. dumosa.	1	0.884 to 0.915	+0° to +6.5°	Cineol.
E. eugenoides.	0.8	0.908	+5°	Cineol.
E. globulus.	1.5 to 3	0.905 to 0.930	+1° to +10°	Cineol; pinene; aldehydes.
E. hæmastoma.	2	0.880 to 0.890	. . . .	Cineol; terpenes, including aromadendrene.
E. leucoxylon.	1	0.915 to 0.927	+0.5° to +2.7°	Cineol.
E. Macarthuri.	. . . .	. . . .	slightly +	Geranylacetate(60%) geraniol; eudesmol.
E. macrorrhyncha.	0.3	0.924 to 0.927 at 22°	. . . .	Cineol; eudesmol.
E. maculata, var. citriodora	1 to 1.5	0.870 to 0.905	To +2°	Citronellal (80%); geraniol; citronellol.
E. microcorys.	1 to 2	0.896 to 0.935	. . . .	Dextro-pinene; cineol.
E. odorata.	1.5	0.899 to 0.925	slightly −	Cineol; cuminal.
E. oleosa.	1.25	0.906 to 0.926	+4° to +5°	Cineol; cuminal.
E. piperita.	0.8	0.909 to 0.913	−3°; +1.6°	Phellandrene; cineol; eudesmol; piperitone.
E. polybractea (Blue Mallee).	. . . .	0.919	−1°	Cineol (60%).
E. punctata.	1	0.912 to 0.920	−1° to +4.4°	Cineol (45 to 65%).
E. Risdoni.	1.35	0.915; 0.916	−5°	Cineol; phellandrene; piperitone.
E. rostrata.	0.1	0.912 to 0.925	−1.1° to +13°	Cineol; valeric aldehyde.
E. Staigeriana.	3	0.880 to 0.901	. . . .	Citral; terpenes.
E. Woolsiana.	0.5	0.889	−13.7°	Aromadendral; cineol (traces).

The oil from *Backhousia citriodora* consists almost entirely of citral (93 to 95%). The oil does not appear to be on the market.

Geranium Oil.   (Rose Geranium Oil.)

The true geranium oil is distilled from the fresh flowering herb of species of *Pelargonium*, chiefly varieties of *P. odoratissimum*, *capitatum*, and *roseum*. Rose petals are not infrequently distilled with the geranium plant to obtain a finer product, so that a true geranium oil is somewhat difficult to procure. The true oils should not be confused with the so-called Indian (Turkish) "geranium" oil (Palmarosa oil), a product of the leaves of *Andropogon (Cymbopogon) Schænanthus* (see p. 303), which is largely used as an adulterant of rose otto.

Geranium oil is colourless or slightly green or brownish and of pleasant rose-like odour. Its sp. gr. ranges from 0.888 to 0.906 at 15.5°, and its opt. rot. between the limits −6° to −16°. The oil is soluble in 3 volumes of 70% alcohol, a factor which is very useful in detecting adulteration.

The following table shows the physical characters of the different commercial varieties of geranium oil (Gildemeister and Hoffmann, *The Volatile Oils*, p. 450). The figures for the German oil are added, though this is not an article of commerce:

Variety	Sp. gr.	Opt. rot.	Solubility in 70% alcohol	Esters (as geranyl tiglate).
French......................	0.897 to 0.905	-7.3 to -9°	2 to 3 vols.	25 to 28
Réunion................	0.889 to 0.895	-8 to -11°	2 to 3 vols.	27 to 33
Algerian................	0.892 to 0.900	-6.3 to -10°	2 to 3 vols.	19 to 29
Spanish................	0.897	-10 to -11°	Not soluble owing to presence of a paraffin	35 to 42
German................	0.906	16°	....	28

Parry gives the following indices of ref. for geranium oils:

African oil...................... 1.4680
Bourbon oil 1.4640
Spanish oil 1.4610
French and German oils 1.4650
Indian oil .... 1.4800 to 1.4900

Geraniol is the chief constituent of geranium oil, which also contains citronellol. The 2 alcoholic constituents of the oil range in amount from 60 to 70% (free), and in addition 20 to 40% of their esters are present, chiefly tiglates. (Detailed information concerning the proportions of the alcoholic constituents, and their estimation and separation, will be found on pp. 259 to 261.) A considerable amount of free acid is sometimes present in geranium oils, while esters of caproic, and probably of acetic, butyric, and valeric acids also occur in small quantities. The Algerian oils contain a smaller proportion of esters than other varieties. In addition, geranium oil contains lævo-menthone, and small amounts of pinene, phellandrene, amyl alcohol, linalol, and a paraffin melting at 63°. Réunion oil is also stated to contain a blue high-boiling fraction, and according to Flateau and Labbé oleic acid is present as the geranyl ester, while other geranium oils are said to contain an acid having the formula $C_{14}H_{28}O_2$.

Geranium oils are liable to adulteration with fatty oils, and with the oils of turpentine and cedar-wood. All such additions tend to decrease the solubility of the oil in 70% alcohol. Fatty oils would be further detected by the presence of a non-volatile residue. The paraffin naturally occurring in geranium oils will rise to the surface

on the addition of alcohol, while fatty oils tend to fall to the bottom of the containing vessel. Geranium oil is largely adulterated with the so-called Indian geranium oil (p. 303), an addition which causes a lowered ester value. An adulteration with benzoic esters has been reported by Schimmel. This raises the ester value and is difficult to detect.

Geranium oil is largely used in perfumery and is known as "rose-geranium" owing to the common practice of adding rose petals to the plants before distillation.

Hyssop Oil.

Examinations of this oil have been made by Schimmel & Co., their latest publication of data being in *Rep.* (Oct., 1909, 69). The oil contains beta-pinene and l-pinocamphone, the latter not hitherto found in essential oils. The analytic data found by Schimmel & Co. are given in above quoted *Report* in comparison with oils examined by Jeancard and Satie (*Amer. Perfumer*, 1909, **4,** 84) as follows. The dates given with J. and S. figures are the years in which the distillates were made. Schimmel & Co. consider that their data were not obtained from oils from the same species of Hyssop as that used by J. and S.

	S. & Co.	J. & S.	
		(1903)	(1908)
Sp. gr. (15°)	0.925 to 0.940	0.9252	0.9262
Opt. act.	−17° to −24° 18′	+1°	−2° 6′
Acid no.	up to 3.1	0.8	0.8
Ester no.	1.4 to 11	9.2	11.9
Ester no. (after acetylation)	37 to 45	70.0	51.1

Juniper Oil.

This oil is obtained by the distillation of the fruit of *Juniperus communis*. The British Pharmacopœia describes the oil as being "distilled from the full-grown unripe green fruit." It has been pointed out by Schimmel & Co. (*Rep.*, Oct., 1898) that the oil distilled on a commercial scale is obtained from the *ripe* fruits, and

that the oil from unripe fruits is in all essential qualities inferior to the normal oil from ripe fruits.

Oil of juniper is colourless or pale greenish-yellow, with a characteristic odour, and a warm, aromatic, bitter taste. The British Pharmacopœia directs that oil of juniper should have a sp. gr. of 0.865 to 0.890, and be soluble, with slight turbidity, in 4 times its volume of 95% alcohol. The United States Pharmacopœia describes the oil as being soluble in 10 vols. of 90% alcohol. The solubility of the oil in alcohol is a valuable aid in testing its purity, but this solubility decreases greatly with age, a fact which should be borne in mind.

The constituents of oil of juniper include pinene, cadinene, a crystalline body, a terpene-alcohol (the so-called juniper camphor), and an ester, probably the acetic acid ester of this terpene-alcohol, b. p. 180°.

The sp. gr. of juniper oil usually ranges from 0.867 to 0.875, and these limits include the majority of samples. The pharmacopœia limits are therefore wide enough to include all genuine oils, and any departure from these limits may be taken as fairly certain evidence of adulteration. Old oils become thick through slow resinification and acquire an acid reaction and a more or less rancid odour. The age of the berries from which the oil is distilled also influences the sp. gr. of the oil.

Juniper oil is lævorotatory to the extent of about −10°. It rarely exceeds this limit, and is usually much less active, ranging from very slightly lævorotatory to about −7°. Gildemeister and Hoffmann state that the oil is sometimes faintly dextrorotatory. Parry gives the ref. index as ranging from 1.4740 to 1.4880. S. & Co. (Rep., Oct., 1909, 72) report a sample with a saponification number of 7.2.

Juniper oil is largely used for the manufacture of "gin-essence" (artificial gin). The true spirit is obtained by the distillation of the fermented juniper-berries, but gin-essence is an article of commerce consisting almost entirely of a solution of juniper-berry oil in alcohol.

Oils from the berries of *Juniperus phœnica* and of *J. oxycedrus* have a lower sp. gr. than the ordinary oil of juniper (0.850 to 0.860). Their opt. activity is similar to that of the ordinary oil of juniper-berries. The *wood* of *J. oxycedrus*, on destructive distillation, yields the oil known as *Cade Oil*.

Fractional distillation serves as a method for the approximate determination of the pinene and cadinene in the oil. Parry states

that with a series of fractionating bulbs, from 25 to 35% of the genuine oil will distil between 155° and 160°, and from 10 to 20% between 270° and 280°. The oxygenated constituents consist in great part of terpineol.

The wood of *J. communis*, when distilled with steam, is said to yield a volatile oil, but it is not an article of commerce. Commercial juniper-wood oil is, according to Parry, either an oil obtained by distilling turpentine oil over the wood or more often a mixture of turpentine with the oil from the juniper-berry. Less frequently it is composed of the waste terpenes from the preparation of so-called terpeneless oil of juniper.

A number of prosecutions have been instituted in England under the Food and Drugs Acts for the sale of "juniper oil" consisting of juniper-wood oil, and for adulteration of the oil with turpentine oil.

Lavender Oils.

The true lavender oil is obtained by the distillation of the flowers of *Lavandula vera*. It is a pale yellow or colourless oil, with a fragrant odour of the flowers and a pungent bitter taste.

The British Pharmacopœia directs that the oil should have a sp. gr. not less than 0.885, and that it should dissolve in 3 volumes of 70% alcohol. J. C. Umney is of opinion that the lower limit for the sp. gr. of English lavender oil should be fixed at 0.883.

The usual English method of distilling lavender oil consists in collecting the last runnings (4 to 8% of the total distillate) apart from the major portion, since toward the end of the distillation decomposition products come over, causing a deterioration in the odour of the oil. The first distillates, as was shown by J. C. Umney's experiments, have a lower sp. gr. (down to 0.881 in recently distilled samples) than the last runnings, which contain a larger proportion of esters.

The 2 chief varieties of this oil are the English and the French. French oil of lavender contains linalol (Bertram and Walbaum, *J. Prakt. Chem.*, 1892, **45,** 590), linalyl acetate (25 to 40%); traces of pinene, limonene and a sesquiterpene; geraniol (probably as esters); cineol; a stearoptene; coumarin; and coumaric acid. English oil differs from the French oil mainly in its percentage of linalyl acetate (7 to 9 or 10% only), and in containing a fairly large proportion of cineol, which imparts a characteristic pungency to the oil.

M. Duyk (*J. Pharm. Chim.*, 1896, [6], **4,** 453) states that lavender

oil contains, in addition to the compounds mentioned in the text, bor-
neol, and its acetic, butyric, and valeric esters.   Bouchardat (*Bul. Soc.
Chim.* [3], 1894, **11**, 147) found dextrocamphene in the oil.   Schimmel
& Co. (*Rep.*, April and October, 1903) have announced the dis-
covery of ethyl-amyl ketone, $C_8H_{16}O$, furfural (in first fractions),
iso-amyl alcohol and an isomeric alcohol, together with esters of the
former, in French lavender oil.

The sp. gr. of both English and French lavender oils varies between
0.885 and 0.900, rarely falling to 0.882.   It increases somewhat with
age.   The addition of alcohol or turpentine oil as an adulterant lowers
the sp. gr., while admixture of spike-lavender or cedar-wood oil raises
this constant.   Schimmel & Co. have observed the adulteration
of lavender oil with resin, the addition of which raises the sp. gr. of
the oil.

"When the oil is shaken with water in a narrow graduated cylinder
its volume should not be diminished (absence of alcohol)."—United
States Pharmacopœia (8th rev.).

The opt. rot. ranges from about —4° or —5° to —10°.   Lavender
oils frequently suffer adulteration with oil of spike-lavender, when the
optical activity is decreased, since the latter is dextrorotatory, +1°
to +5°.   American turpentine oil has a similar effect, while the
lævorotation is also increased by the addition of French turpentine
or cedar-wood oil.   The ref. index, according to Parry, ranges between
1.4620 and 1.4675.

That the odour of lavender oil is dependent on more than one of its
constituents is shown by the fact that the English oil, containing far
less linalyl acetate than French oil, commands a higher price.   Thus
the estimation of the ester content of an oil is not sufficient to decide its
quality, and, in the case of English oils at least, it is necessary to take
into account the purity of the odour as well as the chemical constants
of the samples.   Schimmel & Co. contend that the value of the oil
increases as the ester content rises.   There can be no doubt that the
odour of lavender oil, due partly to the linalyl acetate (which has a
bergamot odour), is modified to a very appreciable extent by other
constituents probably as yet unknown.   Parry is of opinion that no
definite relation exists between the ester content and the perfume
value of French oil of lavender.

The ester content is of value when comparing oils from the flowers
grown in the same district.   The method usually employed is de-

scribed on p. 230. English oils usually contain from 7 to 10% (sometimes 12%) of esters (calculated as linalyl acetate), while French oils contain about 30 to 40% or more. The finest oils produced in the south of Europe are those distilled from plants grown at great elevations. •

The amount of esters present in oil of lavender is lowered by adulteration with either turpentine or spike-lavender oil, neither of which contains any notable amount of esters. Thus, as pointed out by Parry, mixtures of French lavender oil and spike oil can be made, having the same ester content (about 10%) as English oil, but the optical rotation will be lowered and the sp. gr. raised, though not to a very great extent. Much lavender oil is now adulterated with spike oil and ethyl succinate (see below).

Other less important varieties of lavender oil are described in the table on pp. 446 and 447.

The presence of much *cineol* in the oil may be taken as evidence of the presence of spike oil so far as French oil of lavender is concerned, but English oil of lavender contains naturally notable amounts of cineol.

Schimmel & Co. have called attention to the adulteration of lavender oil with ethyl succinate, evidently added to give a fictitious ester value to the oil. 2 samples adulterated with this substance had a high sp. gr. (o.900; o.905), and a high ester value (47.5; 48.5%). These adulterated oils contained approximately 8% of ethyl succinate, which would require about the same amount of alkali for saponification as 18% of linalyl acetate. For the detection of such adulteration, Schimmel & Co. proceed as follows: About 2 grm. of the oil are saponified, and the portion insoluble in water washed out with ether, the aqueous residue neutralised with acid, and diluted up to 50 c.c.; 10 c.c. of cold saturated barium chloride solution are added, the liquid warmed on the water-bath for 2 hours, and then cooled. The formation of any crystalline precipitate is indicative of adulteration, since the barium salts of acetic and butyric acids (the normal organic acids of lavender oil) are soluble.

Ethyl citrate is sometimes used as an adulterant, also for the same purpose as ethyl succinate, *i.e.*, to raise the ester value. The following method, proposed by Schimmel & Co., is stated to be more reliable than the barium method for detecting sophistications by means of added esters:

10 grm. of the oil to be examined are saponified for 1 hour on the water-bath with alcoholic potassium hydroxide solution, the contents of the flask then placed in a porcelain dish and the bulk of the alcohol evaporated. After this the liquid is washed in a separating funnel with about 100 c.c. of water, the oily portions removed by extraction with ether, the aqueous solution returned to the porcelain dish, and the bulk evaporated down on the water-bath. When the alkaline solution has cooled down, it is acidified with sulphuric acid and the organic acids thus liberated absorbed with ether. The ethereal solution is then evaporated in a dish and the residue is heated for some time on the water-bath to remove volatile (acetic and butyric) acids, then cooled, and digested with ether. A fine crystalline residue remains in case of an adulterated oil, which may be identified by m. p., etc.

Salicylic and *benzoic* acids have also been added to lavender oil. There presence is easily detected by the determination of the acid-number. Pure oil of lavender is practically free from acidity.

Spike-lavender Oil.

This oil is obtained by the distillation of the flowering herb, *Lavandula spica*. It is a pale yellow oil, with an odour resembling at the same time lavender and rosemary oils.

True lavender oil contains a notable amount of esters, oil of spike lavender is practically free, but contains a considerable proportion of alcoholic constituents. The composition of spike oil, which has been worked out chiefly by Bouchardat (*C. r.*, 1887, **104,** 551; 1888, **107,** 53), is as follows: Linalol, cineol (a larger amount than English lavender oil), dextropinene, dextrocamphene, camphor, borneol, terpineol, and geraniol. A sesquiterpene is also supposed to be present, and traces of esters of the various alcohols also occur in the oil. The alcoholic bodies, ascertained by the acetylation process and calculated as linalol, usually constitute about 30 to 40% of the oil. The method for the estimation of the alcohols in essential oils is given on page 227. The results are not strictly accurate, on account of the ease with which the alcohols decompose, but valuable comparative results are obtainable.

The sp. gr. of spike lavender oil ranges from 0.904 or 0.905 to nearly 0.920, but it rarely exceeds 0.915. Probably 0.918 should be taken as the maximum limit. Adulteration with turpentine oil lowers the sp. gr.

The optical rotation of spike oil ranges from $-3°$ to $+4°$, rarely up to $+7°$. Oils exceeding a rotation of $+5°$ should be regarded with suspicion. Parry gives the ref. index as 1.4660.

Schimmel & Co. have proposed to fractionate the oil and take the opt. rot. of the first 10% distilled. All spike oils of undoubted purity are stated to give a distinct dextrorotatory fraction, but Parry and Bennett have shown that certain spike oils are not only lævo-rotatory, but may yield a lævorotatory first fraction on distillation. An estimation of the total alcohols is required in these cases to ensure absence of French turpentine oil. An appreciable amount of French turpentine oil will render the fraction lævorotatory. It is necessary, in carrying out this test, to use Ladenburg's flasks of uniform size, and to distil the fraction (5 c.c. from 50 c.c. of the oil) at the rate of not more than one drop per second. The following results were obtained by Schimmel & Co. by the analysis of 4 samples of genuine spike oil:

Number	Sp. gr.	Rotation	Solubility in 70% alcohol	Rotation of first 10% in distillate
1	0.916	$+7°7'$	1 in 3	$+7°11'$
2	0.915	$+3'$	1 in 2	$+5°10'$
3	0.914	$+5°$	1 in 2.5	$+7°11'$
4	0.918	$+5°30'$	1 in 2.5	$+6°7'$

Parry and Bennett lay stress on the importance of examining the fractions obtained by the distillation of spike oil. An adulterated oil examined by them gave a fraction at 230° to 240° consisting of safrol.

Spike oil is soluble in 3 volumes of 70% alcohol. In this form, however, the solubility of spike oil is not of much value as a test for adulteration, since it has been shown by Parry and Bennett (*Chem. and Drug.*, 1903, **63**, 1011) that 25% of certain cheap adulterants may be added to spike oil without altering the solubility in 70% alcohol or the physical characters of the oil. Parry and Bennett suggest therefore that the solubility test should be altered, since it has been found that pure spike oils are soluble in 6 vols. of 65% alcohol. An addition of 5 to 10% of the usual adulterants (common rosemary oil, turpentine oil, and safrol) disturbs this solubility.

Genuine spike oils yield practically no ester value. This figure, together with the sp. gr., opt. rot., rotation of the first 10% distilled, and determination of the free alcohols, are most valuable data for testing the purity of this oil.

Lemon Oil.

This oil is produced chiefly in Sicily and the Riviera, and is probably one of the most complex of the essential oils. It is obtained by expression of the fresh peel of lemons (*Citrus limonum*).

Lemon oil contains dextro- and lævolimonenes, citral (geranial), geraniol, terpineol, geranyl and linalyl acetates, and a crystalline stearoptene (citraptene, consisting chiefly of *limettin* or dimethoxy-coumarin, m. p. 145°. Lævopinene, phellandrene, camphene, methyl anthranilate (Parry), methyl-heptenone, and a resin also occur normally in small quantities, while Burgess and Child have recently shown that octyl and nonyl (and possibly decyl) aldehydes are also present.

Citronellal has been given, but H. E. Burgess states that it is doubtful if genuine oils ever contain it. According to Schimmel & Co., lemon oil also contains a sesquiterpene which is probably lævorotatory.

Limonene is the constituent of lemon oil which occurs in the greatest proportion. The compound to which the odour and strength of the oil is chiefly due, however, is citral. While citral is responsible for the primary odour of lemon oil, the esters geranyl acetate (in Messina and Palermo oils) and linalyl acetate (in Palermo oils), together with small amounts of octyl and nonyl aldehydes and other substances, modify it to such an extent that the purest citral obtainable is but a poor substitute for lemon flavour.

The characters of citral and of citronellal, and the methods for their estimation, are described on pages 270 *et seq.* There has been much controversy as to the normal amount of citral (or rather, of total aldehydes) present in genuine oil of lemon, a standard of 7% being until recently insisted on. It is now acknowledged, at least by most English chemists, that the citral content of pure lemon oil rarely, if ever, exceeds 4%, and is usually lower (3%). This conclusion is based mainly upon the well-known fact that the yield of terpeneless oil of lemon is only 5 to 6% of the original oil, while the concentrated product contains about half its weight of citral. A standard of not less than 4% citral has been adopted in the United States Pharmaco-

pœia, the oil being assayed by a given method. Lemon oil containing
an addition of lemon-grass oil or lemon-grass citral would of course
give a higher aldehyde content.

The method, which is substantially that of S. S. Sadtler (*Amer.
J. Pharm.*, 1904, **74,** 84), is directed by the United States Pharma-
copœia (8th Rev.) to be carried out as follows: Weigh accurately about
15 c.c. of lemon oil into a 150 c.c. flask, add 5 c.c. of distilled water and
a little phenolphthaleïn solution, and exactly neutralise the liquid by the
addition of $N/10$ sodium hydroxide. Add next 25 c.c. of a neutral
solution of sodium sulphite (1 in 5), and immerse the flask in a boiling
water-bath. Run in from a burette as required, with frequent shaking,
sufficient $N/2$ hydrochloric acid to keep the hot liquid neutral. When
the liquid remains permanently neutral, note the c.c. of $N/2$ acid
added. A blank test must be carried out simultaneously. The
number of c.c. of $N/2$ acid obtained by subtracting the volume re-
quired by the blank experiment, from the c.c. of acid used in the
estimation, multiplied by 0.03802×100, and divided by the grm.
of sample taken for the analysis, gives the percentage of citral in the
lemon oil. The method gives useful comparative, if not strictly
accurate, results.

Umney and Swinton (*Pharm. J.* [4], 1898, **7,** 196) have found geranyl
acetate to be present in lemon oil to the extent of 1.2 to 1.4%. This
is true both of the Messina and Palermo varieties of the oil, but in the
latter a small quantity of linalyl acetate is also present.

Lemon oil has probably suffered more from adulteration than any
other essential oil. The adulterants include turpentine oil, lemon
and orange terpenes, distilled orange and lemon oils, lemon-grass oil,
lemon-grass citral, cedar-wood oil, alcohol, and stearin.

The British Pharmacopœia states that lemon oil should have a
sp. gr. of 0.857 to 0.860, and an optical rotation of not less than
59° for 100 mm. It is further directed that the optical rotation of the
first 10% distilled should not differ by more than 2° from the original
oil. The last requirement is based on error, and is met by very few
pure oils. The United States Pharmacopœia (8th Rev.) requires
lemon oil to have an opt. rot. of not less than $+60°$ at 25°. The
error in the rotation of the first 10% distilled, given by the British
Pharmacopœia, is repeated in the United States Pharmacopœia.
The ref. index is from 1.4730 to 1.4750 (Parry).

The sp. gr. of genuine lemon oils ranges between the limits 0.856

to 0.862 or 0.863. These figures are but little altered by admixture with turpentine oil or with turpentine and orange oils, but any addition of alcohol will disturb the sp. gr., and may thus be readily detected. Oils of sp. gr. 0.853, such as have recently been met with, were very possibly adulterated with a small quantity of lemon terpenes.

The opt. rot. of the sample and the fractions obtained by distillation are probably the most valuable figures. Pure lemon oils rarely have a rotation outside the limits $+58°$ to $+66°$, the great majority coming within the limits $+59°$ to $+64°$ at $20°$. The figures differ slightly in different years. According to Burgess and Child, some lemon oils at the earlier part of the season may have a rotation of $+68°$, but such are not usually in the market, and are mixed with lemon oil of a lower activity. The average rotation of Palermo oils is a little lower than that of Messina oils. Schimmel & Co. recommend the distillation of 50 c.c. of the oil in a fractionating apparatus, the first 10% distilled (5 c.c.) being examined in the polarimeter. This fraction should have an opt. rot. lower by not more than $5°$ than that of the original oil (Schimmel & Co.). A small quantity of turpentine oil (5%) has very little influence on the optical rotation of the first 10% of the distillate, since the oil of turpentine does not come over to any great extent at this stage. Parry is of opinion that the examination of the rotation of the successive fractions (in 20% quantities) will yield valuable information. The ref. index of the fractions of lemon oil may yield useful information, but the method possesses no advantages over a polarimetric examination.

About 20 to 30% of lemon oil distils between $172°$ and $174°$.

The addition of turpentine oil to lemon oil causes a decrease in rotatory power, but if an admixture of orange terpenes together with turpentine oil has been made, the rotation of the original oil may not be affected. Careful fractional distillation can alone give definite information with respect to these additions. The apparatus employed should be used also for the distillation of some authentic samples of lemon oil, in order to obtain standard results for comparison. Genuine lemon oil always shows a large increase in opt. rot. of the later fractions over the first 10% distilled. The following table, by Burgess and Child (*J. Soc. Chem. Ind.*, 1901, **20**, 1176) gives the constants and behaviour on fractional distillation of 5 samples of genuine oil of lemon. 100 c.c. of oil were distilled in each case.

CONSTANTS OF PURE LEMON OIL (BURGESS AND CHILD).

	Particulars	Physical constants of original oils		Distillation			Citral content of 3d fraction
				c.c.	Rotation in readings	Zeiss 20°	
I.	Genuine oil of good quality. (Messina.)	Sp. gr. = 0.857 Rotation = +63° 12' Ref. ind. = 1.4755		10 80 7.5	+55° 30' +70° 40' +10° 56'	72.0 72.4 82.5	42%
II.	Genuine oil (Palermo). Not typical.	Sp. gr. = 0.857 Rotation = +61° 27' Ref. ind. = 1.4757		10 80 7.5	+54° 6' +67° 45' +19° 13'	72.2 72.4 81.5	35%
III.	Genuine of very high sp. gr.	Sp. gr. = 0.862 Rotation = +58° 30' Ref. ind. = 1.4771		10 80 7.0	+50° 41' +67° 16' −6° 0'	72.0 72.7 90.6	64%
IV.	Genuine oil of high sp. gr.	Sp. gr. = 0.860 Rotation = +60° 36' Ref. ind. = 1.4769		10 80 7.0	+50° 6' +68° 43' −3° 22'	72.2 72.6 88.6	64%
V.	Genuine oil, new crop, 1901.	Sp. gr. = 0.858 Rotation = +61° 28' Ref. ind. = 1.4754		10 80 7.0	+51° 47' +69° 2' +8° 14'	71.8 72.3 81.9	40%
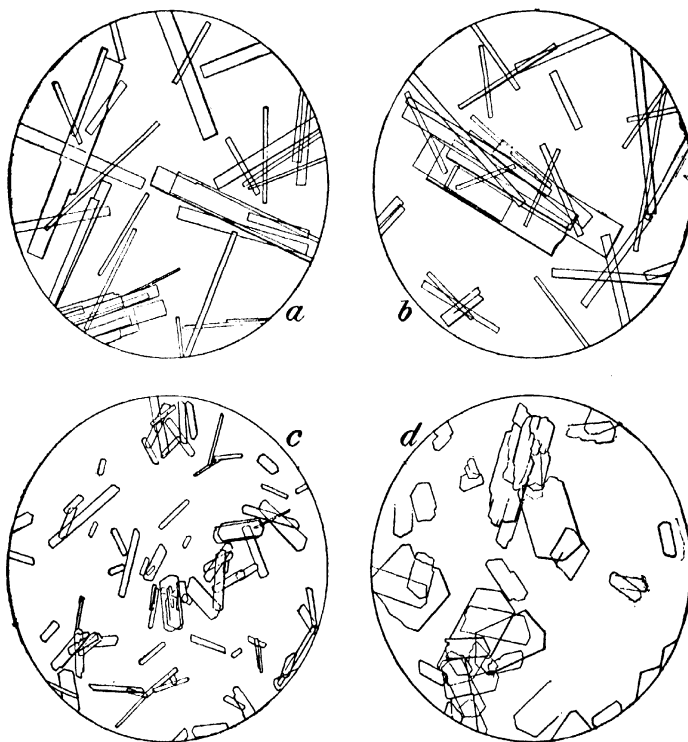
FIG. 5.—Photomicrographs of crystals ×100. a, b, Limonene nitrosochloride from pure lemon oil; c, limonene nitrosochloride and pinene nitrosochloride from lemon oil mixed with 5% of oil of turpentine; d, pinene nitrosochloride from oil of turpentine. Illustrations from Circular 46, Bur. of Chem., U. S. Department of Agriculture, by E. M. Chace.

Pinene in Lemon Oil.

It having been alleged by importers in the United States that lemon oil may naturally contain appreciable amounts of pinene, the subject was carefully investigated by the United States Bureau of Chemistry, and the results published in Circular 46, Oct. 1909, by E. M. Chace.   The investigation showed that genuine lemon oil contains no appreciable amounts of pinene when tested by the following method:

50 c.c. of the sample are distilled as described on page 222.   The

distillate is mixed with an equal volume of glacial acetic acid in a 50 c.c. conical flask and immersed in a freezing mixture. 10 c.c. of ethyl nitrite are added and then, slowly, with constant stirring, 2 c.c. of a cooled mixture of 2 parts of concentrated hydrochloric acid and 1 part of water. The flask is kept for 15 minutes in the freezing mixture, and then rapidly filtered, using a filter-paper disk with vacuum. The resulting crystals of limonene nitrosochloride are dissolved in the smallest possible amount of chloroform and reprecipitated with methyl-alcohol. The crystals are collected, mounted in olive oil, and examined under a power of about 100 diameters. If the pinene derivative is present its crystals are easily detected (see Fig. 5).

The adulteration of lemon oil with orange or lemon terpenes (without addition of turpentine oil) may be inferred from the lowered sp. gr., slightly increased rotation, and in the increase of non-aldehydic constituents. Oils adulterated in this manner have, however, frequently also received an addition of lemon-grass citral. If the oil is distilled *in vacuo*, and the odour of the terpeneless portion observed, the addition of lemon-grass oil or lemon-grass citral will be detected. The optical rotation of this residue may also yield some information. Estimation of the non-volatile matter and of the saponification-number of lemon oil will serve for the detection and determination of added fatty substances. Observation of the ref. index which lies within the narrow limit of 1.473 to 1.475 at 20° is of value.

Lemon oil rapidly deteriorates on keeping. It is best stored in tightly stoppered bottles filled to the neck and kept in a cool, dark place. The turbidity of certain specimens is usually due to a small quantity of water.

Methods for the examination of *lemon flavouring extracts* (essences) and their substitutes have been published by A. S. Mitchell (*J. Amer. Chem. Soc.*, 1899, 21, 1132.

Nutmeg Oil.

This oil is obtained by the distillation of the nutmeg, the fruit of *Myristica fragrans*. It is colourless or pale yellow. It absorbs oxygen, and becomes darker and thicker on exposure to the air.

The British Pharmacopœia (1898) directs that oil of nutmeg should have a sp. gr. of 0.870 to 0.910. It should form a clear solution with its own volume of 95% alcohol, and a little of the oil evapo-

rated on a water-bath should not leave a residue which crystallises on cooling. This ensures the absence of the concrete oil of nutmeg, which may occasionally be carried over in the distillation. Parry has pointed out that the presence (even in traces) of the fixed oil of nutmeg is said to be objectionable in oil of nutmeg used for the manufacture of *sal volatile*. The residue on evaporation of the oil, after purification with alcohol, consists chiefly of *myristic acid*, melting at 54°.

The limits of sp. gr. for this oil, as laid down by the British Pharmacopœia, are regarded by various observers as being too narrow. Schimmel & Co. give the sp. gr. of oil of nutmeg as 0.865 to 0.920, while Parry considers that the limits of 0.868 to 0.915 are not too wide. The ref. index is about 1.4765.

Oil of nutmeg is dextrorotatory, the limits being usually stated as from 14° to 28° or 30°, but Power and Solway (see below) observed a rotation as high as 38.06° in a sample of genuine oil.

The presence of *myristicol* has been noticed by Gladstone and by Wright.

Investigations by Power and Solway (*J. Chem. Soc.*, 1907, **91**, 2037; 1908, **95**, 1653) have shown that the oil contains eugenol, isoeugenol in small quantities with larger amounts of dipentene, dextrocamphene and dextropinene. Several alcohols, as dextrolinalol, dextroborneol isoterpineol, and geraniol, together with safrole and esters of formic, butyric, acetic, and octoic acid, are present in small amounts.

Myristic acid appears to be present to a small extent passing over toward the end of the distillation. It separates on standing. Nutmeg oil that conforms to the b. p. limits is really a fractionated oil, that passing over toward the end of the distillation being rejected for pharmaceutic uses. The highest boiling fractions of the oil appear to contain small quantities of a phenol.

Mace Oil.

This oil is similar to nutmeg oil; indeed, the commercial product is frequently nothing else than oil distilled from nutmegs of inferior quality.

Genuine mace oil is the product of distillation of the arillode of the seed of *Myristica fragrans*. The true oil is colourless, yellowish, or dull red, having a sp. gr. of 0.910 to 0.930 (or, according to Gildemeister and Hoffmann, 0.890 to 0.930). The opt. rot. of the oil is

about $+10°$ or even up to $+20°$. Mace oil is completely soluble in 3 parts of 90% alcohol.

The composition of this oil is very similar to, if not actually identical with, that of nutmeg oil, but the latter appears to contain more terpenes. F. W. Semmler (*Ber.*, 1890, **23,** 1805) found in the higher boiling fractions a crystalline compound forming white needles, m. p. 30°. This substance has, according to the most recent work of Semmler and H. Thoms, the formula $C_{11}H_{12}O_3$, and was named by Semmler *myristicin*.

Nutmeg and mace oils are so similar that they are frequently sold indiscriminately, and it is difficult to obtain authentic samples of either oil.

Orange Oils (Oils of Bitter and Sweet Orange-peel).

The oils of bitter and sweet oranges are obtained by expression from the fresh peel of the fruits of *Citrus bigaradia* and *C. aurantium,* respectively, and are very similar in physical properties and com-position. The oil produced from orange-flowers is known as "neroli oil" (page 366).

Sweet orange oil is an orange-yellow oil with the characteristic orange odour and an aromatic taste. It consists largely (90%) of dextrolimonene (Wallach). The oil contains in addition the following bodies, most of which are present in mere traces or in very small amounts: lævolimonene, pinene (?); citral, citronellal, linalyl acetate, dextrolinalol (Parry), nonylic alcohol, decylic alcohol, dextroterpeneol, normal decylic aldehyde, esters of butyric acid and of its immedi-ately higher homologues (Parry), an ester of caprylic acid, methyl anthranilate or ortho-amido-benzoate (Parry). This substance was found by E. and H. Erdmann and Schimmel & Co. to be present in oil of neroli. It is an oily body having an odour resembling neroli oil. In solution it possesses a fine characteristic fluorescence; and, according to Flatau and Labbé (*Bull. Soc. Chim.*, [3], 1898, **19,** 361) another aldehyde (of unknown composition), myristicol, and myristinic acid. K. Stephan has isolated an acid similar to or identical with cerotic acid. The optical rotation of orange oils differs, more influenced by temperature than is that of lemon oil. These observers also isolated from sweet orange oil an ester (the acid of which contains 21 atoms of carbon; Parry has isolated this

acid, and from an analysis of the silver salt finds that it cannot have
a greater molecular weight, if it is monobasic, than 275; this allows
only 17 atoms of carbon) in the form of an insoluble amorphous pow-
der, melting at 64° to 65°. This compound had a strong odour of
oranges.   K. Stephan denies that orange oil contains either citral
or citronellal.

Bitter orange oil is a yellow liquid with a bitter aromatic taste, and a
delicate orange odour.   It contains limonene, citral, and linalyl acetate.
These are the only constituents that have been recognised with
certainty.

The sp. gr. of sweet orange oil ranges from about 0.848 to 0.852;
that of bitter orange oil from about 0.853 to .0854 at 15°.   The sp. gr.
is not much altered by adulteration with oil of turpentine, but the
addition of alcohol makes a considerable change.   The refractive
index is 1.4725 to 1.4735.   The following physical characters of the
oils have been recorded by Schimmel & Co. and Bush & Co.:

	Sweet orange oil		Bitter orange oil	
	S. & Co.	B. & Co.	S. & Co.	B. & Co.
Sp. gr. at 15°	0.848 to 0.852	0.8495 to 0.8510	....	0.853 to 0.854
Opt. rot. at 20°	+96° to +98°	+96° to +99°	+92° to +98°	+91° to +94°

Also the following S. & Co. (Rep., Oct., 1909, p. 66).

	Sweet orange oil		Bitter orange oil	
	Jamaica	Italy	Jamaica	Italy
Sp. gr. 15°	{ 0.8481 { 0.8488	0.8480 0.8510	0.8517 0.8521	0.8530 0.8570
Opt. rot.	+97°47′ to 98°2′	+95° to +98°	+96°20′ to 96°58′	+90° to +93°
Opt. rot. of first 10 c.c.	+97°4′ to 96°54′	nearly same	+96°40′ to 95°53′	slightly higher
Residuum	1.4%	2 to 4%	2.6 to 3.2%	3 to 5%

Orange oils have a higher optical rotation than any other essential
oil.   Any adulteration must therefore cause a lowering in this constant.
The greatest change is produced by turpentine oil.   Lemon oil lowers
the rotatory power to a smaller extent.   An addition of lemon or tur-
pentine oil to orange oil raises the sp. gr.

To detect turpentine oil use the method on p. 247.

Oil of sweet orange-peel is official in the United States Pharmacopœia, which directs that it should have an optical rotation of not less than +95° and that the first fractions distilled should give no evidence of the presence of pinene.

Pure orange oil begins to boil at about 173° to 174°. Umney found that the pure oil, on fractional distillation, gave 20% of distillate between 173° and 175°; 61% between 175° and 178°; 14% between 178° and 188°; leaving 5% of residue. Admixture with much oil of turpentine will lower the b. p. of the oil.

Distilled orange oil is inferior to the expressed oils, owing to the deterioration consequent upon the distillation process, which injures the oxygenated constituents. Schimmel & Co. give the following figures obtained by the examination of 2 distilled oils of orange:

	Bitter	Sweet
Sp. gr.	0.853	0.855
Opt. rot.	+96.07°	+95.95°

This oil and the residual products from the manufacture of terpeneless oil of orange are occasionally used as adulterants of orange oil. When present in any considerable quantity, both these additions render the colour pale, lower the sp. gr., and affect the odour of the sample. The terpenes of lemon oil are also used as adulterants and have a similar effect.

Oil of orange is acted upon by light and air in the same manner as lemon oil.

The concentrated or *terpeneless oil* of sweet orange is somewhat complex, has a sp. gr. of about 0.900 and an optical rotation of about +10°. At a pressure of 10 mm. terpeneless oil of orange distils between 100° and 150°. Parry found terpeneless oil of orange-pea (immature fruit) to have a sp. gr. of 0.910 and an optical rotation of 6.5°.

Parry has examined a sample of the essential oil obtained from the peel of the immature fruit of the orange, i. e., when about the size of a pea (orange-pea oil). The oil is interesting, since it forms a connecting link between neroli and the fruit oil. The pea oil was found to contain dextro- and lævolimonene, dextrolinalol, and terpineol, and also a trace of methyl anthranilate, but such a small trace of this com-

pound was present that it is clear almost all had disappeared in the
early stage of fructification. The following comparison of the charac-
ters of the oil with neroli oil and the fruit oil is instructive. The decrease
in sp. gr. and increase in opt. rot. show the gradual increase in the
proportion of terpene present:

	Sp. gr.	Opt. rot.
Neroli................	0.870 to 0.880	+4° to +15°
Orange-pea............	0.862	+71° 15′
Orange.......	0.850	+96°

Tangerine orange oil was found by Parry to differ somewhat in
properties from the ordinary orange oils. It is probably identical with
the oil of Mandarin orange. The following table shows the physical
characters and composition of the oils:

	Tangerine orange oil	Mandarin orange oil
Source.......		Expressed peel of C. *madurensis*.
Appearance...		Golden-yellow, with slight bluish fluorescence.
Sp. gr......	0.8589	0.854 to 0.858
Opt. rot....	+70° 48′	+67° to +73°
B. p.........		171° to 175°
Constituents........	A camphoroid (limettin?).	Chiefly dextrolimonene; traces of dipentene, citral (1%) and citronellal; methyl ester of methyl anthranilate; decyl and nonyl aldehydes; linalol; terpineol.

On cooling tangerine oil to a low temperature, fine yellow needle-
shaped crystals separate out. They retain their colour after recrystalli-
sation from alcohol, and melt at 70°. Parry has suggested that this
substance is identical with the "*limettin*" from limette oil, or at least
contains that compound.

According to Parry, mandarin orange oil contains, in addition to the
substances given in the foregoing table, about 1% of the ester found in or-
dinary orange oil by Flatau and Labbé (p. 357). The blue fluorescence
of the oil is stated to be due to the presence of methyl ester of methyl-

anthranilic acid. A valuable paper by Berté and Gulli on the
detection of the adulterants of mandarin orange oil by the observa-
tion of the opt. rot. before and after distillation will be found in the
Chem. and Druggist, 1905, **67,** 445.

Hesse and Zeitschel (*Ber.,* 1901, **34,** 296) have proposed the following
method for the detection and estimation of methyl anthranilate in
essential oils, based upon the precipitation of the ester with sulphuric
acid, and the subsequent saponification. The oil to be examined
is dissolved in 3 parts of dry ether, the solution cooled at least to 0°,
and a cold mixture of 1 vol. of strong sulphuric acid with 5 vols. of ether
is added, drop by drop, with continual stirring, until no further pre-
cipitate forms. The precipitate and any other insoluble matter is
brought into solution by means of alcohol, and the liquid titrated with
N/2 alkali, with phenolphthalein. The solution is then saponified by
boiling with excess of alcoholic potassium hydroxide for 30 minutes.
The quantity of methyl anthranilate may be calculated from the acid
value of the ester sulphate. (It is unsafe to weigh the ester sulphate,
owing to its ready dissociation.) If the precipitate contains princi-
pally the methyl-anthranilic sulphate or analogous compounds, the
amounts of alkali used in the 2 operations will be as 2 : 1. If less
is required in the saponification than is given by this ratio, unsaponifi-
able bases are indicated. These may be extracted by ether from the
alkaline solution. Anthranilic acid is obtained by evaporating the
liquid, acidifying with acetic acid, and extracting with ether. It may
be identified (and its purity confirmed) by the m. p. alone and after
grinding with pure anthranilic acid.

If a large quantity of the sulphate precipitate is obtained it may be
dissolved as above, and an aliquot part of the solution taken for the
titration and saponification. A few drops of sulphuric acid are added
to the main portion of the aqueous solution, which is then shaken once
with petroleum-ether to remove resins. Sodium carbonate solution
is added, the precipitate dissolved in ether and the methyl-anthranilic
hydrochloride precipitated by passing a current of dry hydrochloric
acid gas through the solution. The hydrochloride is purified by solu-
tion in methyl alcohol and precipitation by ether. Other bases forming
soluble hydrochlorides will be found in the etheral solution. The
etheral liquid from the original sulphate precipitate is washed with
water to remove excess of sulphuric acid, and the ether removed. The
liquid may then be used for the detection and estimation of other constit-

uents present in the oil, which will remain unaffected in the above
process.

The following method for the detection and estimation of methyl
anthranilate is due to E. Erdmann (*Ber.*, 1902, **35,** 24). The process
depends upon the formation of an azo-dye when methyl anthranilate,
the only primary base as yet known to occur in essential oils, is diazo-
tised in the presence of an aromatic phenol, such as β-naphthol.
When only very small quantities of the ester are present, a colorimetric
modification of the method is employed, a sufficient amount of an
aqueous solution of β-naphthol-disulphonic acid R being added to the
solution of the ester after diazotisation, and the tint obtained compared
with a standard solution of methyl anthranilate when quantitative
results are required. In the case of larger amounts of the ester,
Erdmann prefers to dilute the diazotised solution of the ester (obtained
by treating its hydrochloric acid solution with sodium nitrite for 10
minutes) to a known volume, and then titrate with it 10 c.c. of a 0.5%
alcoholic solution of β-naphthol (rendered alkaline with caustic soda),
the end-reaction being observed by "spot" tests, or by filtering a
small portion of the liquid and testing it with the diazo-compound
and with the naphthol solution. The insoluble orange-coloured dye
produced falls to the bottom of the vessel, and the titration is finished
when no diazo reaction is obtained either by the addition of a few
drops of the diazo solution or of the β-naphthol solution to a little of the
filtrate from the titrated liquid. A few mg. of methyl anthranilate
may thus be estimated, and the presence of the corresponding com-
pound of methyl-anthranilic acid does not interfere. The colouring
matter above noted dissolved in strong sulphuric acid gives a reddish-
violet solution.

The detection of methyl anthranilate by producing a *quinazoline*
derivative has been described by P. Freundler (*Bull. Soc. Chim.*, [3],
1904, **31,** 882).

A *South American orange oil* has been examined by Umney and
Bennett (*Brit. and Col. Druggist*, 1904, **45,** 169), who found it to
more closely resemble orange-leaf than orange-flower oil. The odour
was very pleasant, and suggested a superior petitgrain oil. As
examined by Umney and Bennett, South American orange oil has a
sp. gr. of 0.887, an opt. rot. of +2° mm., and contains 67% of total
alcohols (as geraniol), of which 38% are free and 35.5% exist as
esters (linalyl acetate). The oil contains lævopinene, dipentene,

furfural, geranyl acetate, linalol and geraniol, terpineol (?) and traces of methyl anthranilate. On fractional distillation at ordinary pressure, 75% of the oil distils between 190° and 220°. The oil is readily soluble in 2 vols. of 70% alcohol. For soap and other perfumery purposes, this oil compares favourably with French petitgrain oil.

Petitgrain Oil.

Petitgrain oil is derived from the leaves, twigs, and usually also the immature fruit of the bitter orange (*Citrus bigaradia*) by distillation with water. A large proportion of the oil now comes from Paraguay.

An oil known as "petitgrain citronnier" is obtained from the twigs, leaves, and unripe fruit of the lemon tree (*Citrus medica*). The oil has an odour similar to that of petitgrain oil, but reminding of lemon. Petitgrain citronnier has a sp. gr. of 0.868 to 0.874 or higher, an opt. rot. of +13° to +34°, and a saponification-number of 14.5 to 32.2. It contains citral and linalyl acetate.

"Petitgrain mandarin" is obtained similarly from *Citrus madurensis*. The oil has an optical rotation of +6.25° and contains about 45% of esters, calculated as linalyl acetate.

Petitgrain oil is a yellowish oil with an aromatic and slightly bitter taste, and an odour similar to that of neroli oil, though far less delicate than the latter. Petitgrain oil is completely soluble in 2 volumes of 80% alcohol, and usually in 3 to 4 volumes of 70%.

The sp. gr. of petitgrain oil usually ranges from 0.885 to 0.900, though some samples may fall to 0.882. French oils have generally a lævorotation, but those from Paraguay are mostly dextrorotatory. The limits are about −1° to +4° or +5°. The oil has a saponification-number of 110 to 245, equivalent to 38 to 85% of ester calculated as linalyl acetate. The ref. index is about 1.4650.

Petitgrain oil as usually met with (*i. e.*, derived from the leaves, twigs, and immature fruit) contains among other substances dipentene, dextrolimonene, furfural, lævolinalol (25 to 35%), nerol, geraniol, dextroterpineol (m. p. 35°), linalyl acetate (50 to 75%), geranyl acetate, neryl acetate, methyl anthranilate (small amount) a sesquiterpene, and a pyrrol derivative. Oils which have been obtained from the leaves and twigs (only) of the plant contain little or no limonene. Petitgrain oil obtained only from the leaves of the tree contains 70 to 75% of linalol, 10 to 15% of geraniol, and a small proportion of a sesquiterpene.

Orange-flower Oil (Neroli Oil).

This oil is obtained by the distillation of the flowers of the bitter orange, *Citrus bigaradia*, with water. It is really the oil that separates directly from the water in the distillate (without cohobation), and is a by-product in the manufacture of orange-blossom water, which latter is official in the British and United States Pharmacopœias.

Neroli oil is yellowish, slightly fluorescent with a powerful odour of orange-blossoms, and a bitter aromatic taste. It becomes brownish-red on exposure to light for some time. When strongly cooled, it becomes turbid by the separation of a stearoptene, termed by Boulay in 1828 "neroli camphor." It is an odourless and tasteless paraffin melting at 55°.

Neroli oil has a sp. gr. ranging from 0.870 to 0.880 (usually 0.870 to 0.875), and is slightly dextrorotatory, about +1.5° to +5.0°, or slightly higher. The ref. index is given by Parry as about 1.4750. It is soluble in 1.5 to 2 volumes of 80% alcohol, the resulting solution having a violet-blue fluorescence (due to methyl anthranilate). The addition of more alcohol to this solution causes a turbidity, and crystalline flakes of the paraffin separate out. The physical properties of neroli oil, together with a comparison of the odour with oils of known origin, are valuable data in judging of purity.

An oil produced by the simple distillation of the flowers of *Citrus aurantium*, sometimes termed "*sweet neroli oil*" or *Portuguese neroli oil*, is occasionally met with, though the commercial specimens of the oil sold under these names are usually derived from a mixture of various aurantiaceous oils. A sample of the true "sweet neroli oil" distilled in Germany had a sp. gr. of 0.893 and an optical rotation of +16.1°. It is a dark yellow oil having an odour altogether unlike the true neroli and orange oils.

Commercial oil of sweet orange-flowers has a sp. gr. of 0.860 at 23°, and an optical rotation of about +30° at the same temperature. 1 sample contained 6.35% of esters (as linalyl acetate), and no methyl anthranilate could be detected. According to E. Theulier, the oil contains, in addition to esters, dextrocamphene, dextrolimonene, dextrolinolol, and a paraffin.

The *constituents* of neroli oil comprise limonene; lævopinene; dipentene; lævolinalol (20 to 25%); geraniol; nerol; dextroterpineol (m. p. 35°); dextronerolidol (6%); linalyl, geranyl and neryl acetates (7 to 18%); esters of phenyl-acetic acid; benzoic, acetic, and palmitic

acids (traces); methyl anthranilate (0.7%); indol, and a paraffin. The odour of the oil and its characteristic fluorescence are largely due to the presence of methyl anthranilate.

Nerol and *nerolidol* are alcohols identified by Hesse and Zeitschel in neroli and petitgrain oils. Nerol is isomeric with geraniol, and possesses a delicate odour of roses. It does not combine with calcium chloride, as does geraniol. Nerolidol is a sequiterpene alcohol, probably belonging to the aliphatic series. It has a feeble odour and the low sp. gr. of 0.880.

Indol and *methyl anthranilate* have been shown by Hesse and Zeitschel to be present in orange-flowers, and they are thus not accidental products of the process of manufacture.

Methyl ortho-amino-benzoate, or methyl anthranilate, was discovered in neroli oil by E. and H. Erdmann and Schimmel & Co., and is an oil which crystallises on cooling. This substance has been found by Parry in bitter orange oil, the crystals melting at 23° to 25°. It is interesting as being almost the only nitrogenous constituent of essential oils possessing a sweet odour. The artificial neroli oil of commerce consists chiefly of methyl anthranilate with several alcohols, and is a frequent adulterant of the natural oil. Nerolin, a crystalline synthetic body, is β-naphthol-methyl-ether.

The *adulterants* most usually found in neroli oil are the oils of bergamot and petitgrain. Since linalol and linalyl acetate are characteristic constituents of all these, the detection of them in neroli oil is rendered somewhat difficult. Oil of bergamot, however, usually contains from 35 to 45% of esters, with a corresponding saponification-number of 100 to 130, while petitgrain oil contains 35 to 85% of esters, with a corresponding saponification-number of 110 to 245. Genuine neroli oils shows a saponification-number ranging from 20 to 52, corresponding to 7 to 18% of esters, but good oils usually have saponification-numbers lying between 35 and 45, equivalent to 12 to 15% of esters (as linalyl acetate). Thus an oil having a saponification-number exceeding 55 should be regarded as suspicious. The acetyl-number of neroli oil is about 160, equivalent to 35 to 38% of free alcohols.

It is probable that an appreciable saponification of the esters of neroli oil (to the extent of 5 or 6%) takes place during distillation, as is known to occur in lavender oil distillation (Jeancard and Satie, *Bull. Soc. Chim.* [3], 1900, 23, 605).

Distilled oil of orange, distilled over orange-blossoms, is also fairly frequently met with as an adulterant of neroli oil.

The proportion of stearoptene present in neroli oil depends upon the extent to which the distillation of the blossoms is carried, the later fractions of the distillate containing most of the paraffin. The adulteration of neroli oil with stearoptene-free oils of course lowers the content of stearoptene and thus the strongly cooled oil may not become turbid, as would be the case with an oil containing a normal amount of the paraffin. This fact has been employed as a test for the genuineness of neroli oil.

Chinese neroli oil is stated to be derived from *Citrus triptera* (*Trifoliata*). An examination of this oil by Umney and Bennett (*Pharm. J.* [4], 1902, **15,** 146) showed that it is of a yellowish-brown colour, becoming paler on exposure to light. It has a sweet odour and is slightly fluorescent, especially in alcoholic solution. The sp. gr. of Umney and Bennett's sample was 0.850, and it had an opt. rot. of $+35°$. The oil contained 4.8% of esters calculated as linalyl acetate, and 21.4% of free alcohols (as linalol). It consisted chiefly of limonene, linalol, traces of linalyl acetate, methyl anthranilate, and a paraffin.

Orange-flower water is usually obtained by the distillation of the flowers either with steam or water over an open fire. Neroli oil and orange-flower water are obtained. The water reproduces the odour of the flowers much better than the neroli oil.

About one-third of the odoriferous constituents (the most valuable) the blossoms pass into the water. Except for the terpenes, orange-flower water contains the same constituents as neroli oil, together with esters of phenyl-ethyl alcohol and, possibly, phenyl-aceto-nitrile. The proportions of free alcohols and of methyl anthranilate are much higher in the oil contained in orange-flower water than in neroli oil, while the esters of the terpene-alcohols are much less in amount. Orange-flower water is official in the British and United States Pharmacopœias.

Parsley Oil.

This oil may be obtained by the distillation of any part of the common parsley herb (*Petroselinum sativum*). It is usually distilled from the seeds, but the finest oil is that obtained from the green herb.

The characters of parsley oil as obtained from different parts of the

herb are shown in the following table. The specific properties and composition of French oil of parsley are also included:

Source	Sp. gr.	Opt. rot.	Other characters and constituents
Seeds.	1.05 to 1.10	− 5 to − 10°	A colourless, yellowish or yellow-green thick oil, containing lævo-pinene and apiol.
Green leaves	0.900 to 0.925	+ 0.2 to + 5.2°	Thin greenish-yellow oil, containing about 20% apiol.
Dried root . . .	1.049	Dextrorotatory	Apiol crystallises out at ordinary temperatures.
French oil	1.017	− 5.7°	Palmitic acid (?); mixture of several phenols; pinene; myristicin; apiol. Myristicinic acid formed on oxidation.

Parsley oils containing much apiole (frequently called "parsley camphor") often become semi-solid, or deposit crystals, at the ordinary temperature. The apiole can be crystallised out from any oil containing it by cooling to a low temperature.

Apiol has the constitution of a dimethyl-methylene-ether of allyl-tetroxy-benzene. An isomer of this substance, dill-apiol, is present in oil of dill. The constitution and characters of these substances are discussed on pp. 299 *et seq.*

Parsley oil has been found by Mourgnes and by Bignami and Testoni (*Pharm. J.* [4], 1900, **11,** 313; *Pharm. Zeit.*, 1900, **45,** 606) to contain another constituent or mixture of constituents, to which Mourgnes gave the name "cariol." According to Bignami and Testoni, about 50% of this substance consists of a compound possibly identical with the "myristicin" found by H. Thoms to be the chief constituent of French parsley oil (with some apiole), apiole being, according to this observer, the preponderating constituent of German parsley oil. Thoms considers this compound, isolated by him from French parsley oil, to be true myristicin, while the similar compound in mace oil (p. 359) he regards as *iso*-myristicin.

Peppermint Oil.

The English and American forms of this oil, which is official in the British and American Pharmacopœias, are obtained by the distillation with steam of the leaves and flowering tops of the herb *Mentha piperita*. The English oil is prepared from the green herb, while the best kind of American oil (from Wayne County, New York) is frequently obtained

from the dried or partially dried herb.   Japanese and Chinese oils
of peppermint are derived from *Mentha arvensis.*

2 varieties of the herb—known as black and white mint—are
used in England for the production of oil of peppermint.   The black
mint is the coarser kind and yields more oil, of somewhat less delicate
aroma, than the white mint.   Peppermint oil is much used in medicine
and pharmacy, and in the preparation of confectionery and liqueurs.

J. C. Umney found 2 oils from "black" and "white" mint to
have the following characters:

| Source | Sp. gr. | Opt. rot. | Menthol, % | | Menthone, % |
			Free	Combined	
Black mint............	0.9036	−23.5°	59.4	3.7	11.3
White mint...........	0.9058	−33°	51.9	13.6	9.2

The British Pharmacopœia describes peppermint oil as colourless,
pale yellow, or greenish-yellow when recently distilled, becoming
gradually darker by age.   The British Pharmacopœia directs that the
oil should have a sp. gr. of 0.900 to 0.920, and should dissolve in 4
volumes of 70% alcohol.   It is further directed that if a portion of
the oil be cooled to 17° F. (= −8.3°) and a few crystals of menthol
be added, a considerable separation of menthol should take place.

English oil of peppermint is probably the finest in odour, although
certain German distillates approach it in this respect.   The odour and
taste of the oil are very good guides to its quality.   Peppermint oil
improves in odour on keeping, even for many years.   Japanese oil of
peppermint is at the ordinary temperatures frequently a mass of
crystals (menthol) saturated with oil.

American oil of peppermint is the only variety of this oil the com-
position of which is at all fully known, but so far as the other kinds
have been examined, they have been found to closely resemble the
American, and this is especially the case with the English oil.   Amer-
ican oil of peppermint was the subject of an exhaustive research
by Power and Kleber (*Arch. Pharm.*, 1894, **232,** 639), who found
it to contain the following bodies: menthol, menthyl acetate, menthyl
isovalerate, a menthyl ester, menthone, acetic aldehyde, acetic acid,
isovaleric aldehyde and acid, inactive pinene, lævolimonene,

phellandrene, cadinene, cineol, a lactone, traces of amyl alcohol
and dimethyl sulphide, and some unstable high-boiling sulphur com-
pounds. In addition, peppermint oil possibly also contains liquid
isomeric menthols. The composition and quality of the oil are
considerably influenced by the climate and soil, and the cultivation
methods employed.

P. Charabot has shown that during the development of the pepper-
mint plant, an oil rich in menthol is first formed containing only a
little ester and menthone. Later, the development of the green parts
causes a diminution in the total menthol in the oil, while the esters
increase in the leaves and diminish in the flowering part of the plant.
Finally the menthone increases in the flowers by the oxidation of
menthol. The esterification is confined to the green parts of the plant.

The *sp. gr.* of pure English oil of peppermint is generally well within
the British Pharmacopœia limits, ranging usually from 0.906 to 0.909.
Some pure specimens exceed these narrow limits, while very rarely a
sp. gr. of 0.925 is reached. American oils have sp. gr. ranging from
0.910 to 0.920, while the density of French oils ranges from 0.918
to 0.921. German oils show a still higher sp. gr. Japanese oil
from *Mentha arvensis* has usually a sp. gr. of 0.895 to 0.900 at 24°.

The *opt. rot.* of English peppermint oil usually ranges from −27°
to −32° (United States Pharmacopœia limits = −25° to −33° at 25°)
falling very rarely to −10° or lower. The rotation is least in the case
of South Italy and French oils (about −5° to −10°) and greatest
with the Japanese variety (up to about −43°). This constant is of
much value in conjunction with sp. gr. for the detection of adultera-
tion. The ref. index is about 1.4650.

The table on the next page shows the characters of normal pepper-
mint oils from various sources.

Valuable figures relating to the physical characters and chemical
composition of the various peppermint oils of commerce have been
recorded by J. Lifschitz (*J. Soc. Chem. Ind.*, 1901, **20**, 151); Italian
oils, C. E. Zay (*Chem. Centr.*, 1903, **1**, 331); while Umney and Bennett
have described the characters of Sicilian oils obtained from the black
Mitcham peppermint herb grown in Messina (*Chem. and Drug.*
1905, **67**, 945).

The solubility test for peppermint oil described in the British
Pharmacopœia is not always fulfilled by pure oils (p. 373). Many
samples will dissolve in 4 volumes of 70% alcohol with at most a

trifling opalescence, but the best kinds of American oil (from the dry herb, for instance) are not fully soluble in alcohol of this strength. All peppermint oils are soluble in half or more volumes of 90% alcohol.

The United States Pharmacopœia requires peppermint oil to be rectified and free from dimethyl sulphide, the presence of which may be recognised by the formation (after a short time) of a white film at the zone of contact when the first c.c. of distillate from 25 c.c. of the oil is poured on to a little mercuric chloride solution.

The normal composition and properties of the chief varieties of peppermint oil are given in the table on page 373. Japanese oil contains naturally a very high proportion of menthol—frequently as much as 85% ₍—and dementholised (or partially dementholised) Japanese oil (by freezing) is sold sometimes as such, and sometimes as the pure oil. Dementholised Japanese oil has a sp. gr. of 0.895 to 0.905 at 15°. English peppermint oil contains about 55 to 70% of menthol (free and combined), or somewhat more than the proportion found in most American oils. With Japanese oils, a considerable separation of menthol takes place at the ordinary temperature. American oil generally sets quite solid when placed in a freezing mixture, while English and German oils usually only deposit crystals after long standing in a freezing mixture. For this reason the British Pharmacopœia test for the presence of a due proportion of menthol, based on the separation of the crystals as already described, is no criterion of the value of the oil. The United States Pharmacopœia (8th Rev.) requires peppermint oil to contain at least 8% of ester (as methyl acetate) and 50% of total menthol (free and combined), when assayed by the saponification and acetylation processes (see below).

Owing to its importance and high price, peppermint oil is extensively adulterated. An examination of the physical constants of the oil will serve to detect such additions as alcohol, and turpentine and some other oils. All adulterants cause a diminution of the menthol content, which should therefore be determined. The methods for the estimation of the free and combined menthol, by saponification and acetylation, and for the estimation of menthone, by reduction with sodium to menthol and the subsequent determination of the alcohol formed, are fully described on page 227. The alcohol solubility figures are valuable, since it is frequently possible to determine the source of the oil by their means. In many cases where the oil is

CHARACTERS OF NORMAL PEPPERMINT OILS.

	American		English [Mitcham]	French	Russian	Japanese	Saxon (and best German)	Italian (refined) 1 sample
	Wayne County	Michigan						
Botanical origin....	Mentha piperita.	Mentha piperita.	Mentha piperita.	....	....	Mentha arvensis.	....	....
Sp. gr...........	0.910 to 0.920	0.905 to 0.913	0.900 to 0.910	0.918 to 0.921	0.905 to 0.915	0.895 to 0.900 at 24°	0.900 to 0.915	0.912
Opt. rot........	-25 to -33	-18 to -29	-22 to -33	-6 to -8.5	-17 to -22	-25 or -30 to -43	-25 to -33	-16.3
Solubility in alcohol, 70%.	Not clearly soluble.	Sol. 1 in 5.	Sol. 1 in 3 to 5.	Insol. (1 sample).	....	Sol. 1 in 3 to 5.	(Fresh herb), sol. (Dry herb), insol.	Sol. 1 in 7.
Iodine absorption.	....	....	58	....	....	....	....	147
Solidification-point?	Solid mass of crystals.	....	....	....	....	+17 to +28	....	....
Ref. index at 20°.		1.4635						1.4680 at 16°
Effect of freezing.	Solid mass of crystals.	Solid mass.	Some crystals on long standing.	....	Some crystals on long standing.	At 15° mass of crystals saturated with oil.	Some crystals on long standing.	Does not congeal.
Total menthol, %.	50 to 60	60	58 to 70	44 to 46	50	70 to 91	55 to 68	55.5
Free menthol, %.	40 to 45	50	50 to 60	36 to 40	47	65 to 85	46 to 61	45.8
Combined menthol, %.	8 to 14	10	3 to 14	5 to 10	3:14	3 to 6	6 to 8	9.7
Menthone, %. ...	12	....	9 to 12	8.8 to 9.6	(?) 35 to 40	....	16	8

insoluble in 70% alcohol, a low menthol content will be found. It has been stated that some oils, otherwise pure, have received an addition of menthol itself, which is frequently cheaper than oil of peppermint.

The behaviour of peppermint oils on distillation is a useful test as to genuineness. The published data differ to some extent being influenced according to the method of distillation employed. All genuine oils will yield a considerable fraction distilling in the neighborhood of 215°, since menthol boils at 212°. The following is a summary of the results of distillation (50 c.c.) of 17 pure peppermint oils from various sources, recorded by Schimmel & Co.:

Temperature	Distillate, %
Up to 200°	1.0 to 8.8
200°–205°	0.6 to 19.2
205°–210°	2.4 to 26.8
210°–215°	13.0 to 49.4
215°–220°	6.4 to 34.4
220°–225°	0 to 23.6
225°–230°	0 to 9.6
230°–235°	0 to 6.2
Residue,	4.2 to 17.4

Peppermint oil adulterated with light camphor oil will be found to give abnormally large fractions between 200° and 205°. Parry and Bennett (*Chem. and Drug.*, 1903, **63**, 154) isolated from many samples of adulterated oils a high boiling fraction (258° to 268°) consisting mainly of cadinene, and diceded that the adulterant was African copaiba oil. Such an addition lowers the rotatory power (or the sample may even be dextrorotatory), raises the refractive index, and of course lowers the menthol content.

Another adulterant of oil of peppermint, identified by Bennett (*Chem. and Drug.*, 1903, **62**, 591), is purified "acetin," a mixture of the 3 (mono-, di , and tri-) propenyl acetates, which was present to the extent of about 15%. The adulterant was obtained in the residue after distillation under reduced pressure. This residue was optically inactive, and had a sp. gr. of 1.166 and a ref. index of 1.4355. A sample of the mixed acetins prepared by Bennett had a sp. gr. of 1.187 and a ref. index of 1.4442. Pure oil of peppermint gives no

fraction having a higher sp. gr. than about 0.960, nor ref. index much outside the limits 1.461 to 1.479. Oils containing triacetin do not respond to the alcohol solubility test, since although soluble at first, on addition of more 70% alcohol oily drops separate on standing.

Parry and Bennett also detected (*Chem. and Drug.*, 1904, **64,** 854) adulteration of peppermint oil with cedar-wood oil. 3 samples showed a sp. gr. of 0.908, an opt. rot. of —24°, a refractive index of 1.4670 at 20°, and a total menthol content of 48 to 49%. The oils were insoluble in 70% alcohol, from 30 to 50% floating on the surface of the liquid. Fractional distillation revealed the presence of cedar-wood oil by the increasing sp. gr., optical rotation, and index of refraction of the later portions of the oil. By refractionation of the last 5% distilled, Parry and Bennett obtained fractions showing sp. gr. ranging from 0.914 to 0.933; opt. rot. —40° to —45°, and ref. index, 1.470 to 1.500. Some of these fractions had a distinct cedar-wood taste.

African copaiba oil, which is also used as an adulterant, alters the physical characters in the same manner as does cedar-wood oil.

Several colour tests of peppermint oil have been described, but these are of little use as tests of purity. The best known is that produced by glacial acetic acid with English and American oils. Japanese oil does not respond. When about 5 drops of the oil are mixed with 1 c.c. of glacial acetic acid, a blue is obtained (after several hours), which gradually increase in intensity up to 24 hours. With American peppermint oil a dark blue is seen when viewed by transmitted light, and a fine copper-coloured fluorescence with reflected light. The English oil gives a similar though less pronounced result. Slight warming of the mixed liquid accelerates the action, a violet-blue resulting. The effect is due to oxidation, since it only takes place in presence of air. Oils previously exposed for some time to sunlight do not give the colour. (See further P. Welmans, *Pharm. Zeit.*, 1901, **46,** 591.)

The reaction may be very quickly produced by operating in the manner described in the United States Pharmacopœia (1890). 2 c.c. of the oil is mixed with 1 c.c. of glacial acetic acid and 1 drop of nitric acid. Under these conditions even Japanese oil gives a slight violet.

Spirit of Peppermint and essence of peppermint, for which the pharmacopœial preparation is generally supplied, is a solution of 1 part by measure of peppermint oil in 9 parts of 90% alcohol.

Spearmint Oil.

The British Pharmacopœia describes this oil as being obtained by distillation from the fresh flowering spearmint, *Mentha viridis*. American oil is obtained from this source, whilst the German oil is obtained from *M. crispa*. The botanical source of Russian spearmint oil is doubtful.

Spearmint oil is colourless, pale yellow, or greenish-yellow when recently distilled, becoming darker with age. It has the odour and taste of the herb. The British Pharmacopœia states that the oil has a sp. gr. of 0.920 to 0.940, and forms a clear solution with its own volume of 95% alcohol. With 80% alcohol the oil forms a clear solution in equal volumes, but turbidity is produced on further dilution with the alcohol (United States Pharmacopœia, 8th Rev.).

The following table shows the characters of several oils of this class, based mainly on the results of Schimmel & Co. Only the first 2 are of practical importance:

Kind of oil	Botanical source	Sp. gr.	Opt. rot., °	Other characters
American...	*Mentha viridis.*	0.920 to 0.940	− 36 to − 48	Sol. in equal vols. of 90 % alcohol. Contains lævocarvone and lævo-limonene, etc.
Russian	*M. aquatica (?).*	0.880 to 0.890	− 20 to − 25	Sol. in 2 vols. 70% alcohol. Contains lævo-carvone; lævolinalol; lævolimonene; and cineol.
Horsemint..	*M. aquatica.* *M. Canadensis.* *Monarda Punctata.*	0.880 to 0.890 0.940 0.930 to 0.940	+ or − .... Slightly +	Contains terpenes; cymene; thymol; linalol (?); traces of acetic, butyric, and other fatty acids.

Oil of spearmint contains lævopinene, lævolimonene, carvone, and probably small amounts of linalol and other substances. The proportion of carvone ranges from about 35 to 55%. It may be estimated as described on page 214. Russian oils appear to contain cineol.

Schimmel & Co. have described a spearmint oil (distilled by them in America) which had a sp. gr. of 0.980 and an optical rotation of ---42.5°. It appeared to contain an abnormally large amount of carvone.

Pennyroyal Oils.

True pennyroyal oil is from the herb of *Mentha pulegium;* American oil from the herb of *Hedeoma pulegioides.*

The true oil is yellow or reddish-yellow with a strong odour.   The sp. gr. is usually within the limits 0.930 to 0.960, but Umney and Bennett (*Pharm. J.*, [4], 1905, **21,** 860) reported a sample of Sicilian provenance with a sp. gr. 0.927 at 15° and an optical rotation of +35. The usual optical rotation is from +17 to +23.   The refractive index is about 1.4800 (Parry).

The oil is soluble in 2 or more volumes of 70% alcohol.

Pennyroyal oil contains menthol, pulegone, α- or β-isopulegone (possibly), menthone, and terpenes (probably lævolimonene and dipentene). About 80% of the oil distils between 212° and 216°.   Adulteration with turpentine oil lowers the sp. gr. and b. p. of pennyroyal oil, while it is less soluble in alcohol when this adulterant is present.

A Russian oil derived from *Pulegium micranthum* has a sp. gr. of about 0.930.

The composition of American pennyroyal oil has been closely studied by Barrowcliff (*J. Chem. Soc.*, 1907, **91,** 875) who found the principal constituents to be lævomenthone and dextro-isomenthone (together, about 50%); pulegone, about 30%; 1-methyl-3-cyclohexanone, 8%; with lævopinene, lævolimonene, and dipentene in small proportions. A sesquiterpene alcohol was present in a proportion of about 2%, and a small proportion of methyl salicylate.

The oil examined had a sp. gr. of 0.9297 at 15°/15°, an opt. rot. of 25.73°, and was soluble in twice its volume of 70% alcohol.

Schimmel & Co. give 0.925 to 0.940 as the limits of sp. gr.

Pimento Oil (Allspice Oil).

This oil is obtained by the distillation of the dried unripe fruit of *Pimenta officinalis.*   It is yellow or yellowish-red becoming gradually darker.   It has the odour and taste of pimento, which resembles a mixture of cinnamon, nutmeg, pepper, and cloves, the last mentioned predominating.   Hence the name "allspice."

The British Pharmacopœia gives the sp. gr. of pimento oil as not below 1.040.   It states that "the oil should be converted into a semi-solid mass when shaken with an equal volume of strong solution of

ammonia." In the United States Pharmacopœia, strong sodium hydroxide solution takes the place of ammonia.

Schimmel & Co. give the limits of sp. gr. of this oil as 1.024 to 1.050, and state that the b. p. limits require correction. The experience of English chemists, however, agrees with the limits laid down by the Pharmacopœia, and it seems improbable that an oil of 1.024 sp. gr. contains a due proportion of eugenol.

Pimento oil consists for the most part of eugenol, which is present to the extent of about 65 to 70 (or even 80)%. In addition, the oil contains cineol, lævophellandrene, methyl-eugenol, etc. A sesquiterpene is also present, but its exact nature has not yet been fully ascertained. The odoriferous body or bodies are unknown. The oil closely resembles oil of cloves in composition and properties.

The sp. gr. of genuine oil of pimento usually ranges from 1.040 to 1.055. The optical rotation ranges from --1° or --2° to --4°.

Fractional distillation is a valuable aid in judging of the purity of this oil. The sp. gr. is higher according as the eugenol content is higher, and the fraction distilling over between about 245° and 250° should be large, as it contains the whole of the eugenol, b. p. 247°. The proportion of eugenol, as determined by Thoms' method (page 295), should be at least 60 to 65%. The United States Pharmacopœia (8th Rev.) requires the oil to contain at least 65% by volume of eugenol when assayed by Umney's process (see page 294).

Oil of pimento is soluble in all proportions in 90% alcohol, and also in 2 volumes of 70% alcohol.

Oil of pimento leaves is described by Gildemeister and Hoffmann as having a sp. gr. 0.882 at 25°, and an opt. rot. of --0.6°. It contains citral.

Pine-needle Oils.

Under the above title are comprised the volatile oils of the needles and young shoots of many coniferous plants. They are colourless liquids of balsamic odour. In composition they are in a strongly marked contrast to the different forms of turpentine oil, yielding only a small percentage of distillate below 170°. A characteristic constituent of pine-needle oils is bornyl acetate, though other esters of borneol may be present in some varieties. Pine-needle oils contain several terpenes, mostly lævorotatory, among which lævo- and dextropinene, lævo-

limonene, dipentene, phellandrene and sylvestrene have been recognised. The table on pages 380 and 381 shows the characters of the chief pine-needle oils, the data being taken from the researches of Bertram and Walbaum (Schimmel & Co., *Rep.*, Oct., 1892; *Arch. Pharm.*, 1893, **231**, 290) and from the results of Gildemeister and Hoffmann (*The Volatile Oils*). The characters of certain factitious oils examined by the first-named observers are also included in the table.

From the figures it appears that pure pine-needle oil yields on distillation only a moderate fraction below 170°, and leaves a considerable portion undistilled at 185°. This residue consists chiefly of bornyl acetate with other esters of borneol.

Sample 4, a pine-twig oil from *Abies excelsa* or *pectinata*, contained no appreciable quantity of borneol or its derivatives (0.5%), the oil consisting almost entirely of lævopinene and lævolimonene, which latter constituent was recognised by the m. p. of the hydrobromide (104°).

The so-called American hemlock or spruce oil (12) contained 36% of bornyl acetate, the other constituents being lævopinene and a sesquiterpene (cadinene).

Pumilio oil (pine oil), which is official in the British Pharmacopœia (1898), contains smaller proportions of pinene and borneol derivatives, but the presence of phellandrene is indicated by the ready formation of its nitrite. Sylvestrene and cadinene are also present. In the Austrian Alps, the needles and branches of *P. pumilio* are distilled on a large scale, and the oil obtained is used extensively in soap-making and perfumery. A sample of 0.865 sp. gr., and −9° rotation contained lævopinene and lævophellandrene, sylvestrene, bornyl acetate (5%), and cadinene. The oil produced in Sweden from the needles of *P. sylvestris* (No. 8 in table) contained dextropinene, sylvestrene, and probably some bornyl acetate. The German oil from the same tree had a similar composition.

The oil from *Pinus sylvestris* was official in the British Pharmacopœia (1885). The oil from *P. pumilio* replaced it in the 1898 edition, since the former oil is not now met with in commerce. Not more than 10% of pumilio oil should distil below 165° (British Pharmacopœia, 1898). The Pharmacopœial limits for sp. gr. (0.865 to 0.870) are somewhat too narrow.

Bertram and Walbaum state that pinene is generally present in pine-needle oil, but that while the oils from *Abies picea* contain chiefly

CHARACTERS OF PINE-NEEDLE OILS.

	Sp. gr., 15.5°	Opt. rot.,°	Solubility in alcohol (90%)	Esters as bornyl acetate, %	Behaviour on distillation			
					First distillate at	150 to 170°, %	170 to 185°, %	Residue, %
Genuine Pine Oil.								
1. From needles and twigs of *Picea vulgaris* (Norvegian spruce).	0.880 to 0.888	−21.7 to −37	....	8.3 to 9.8	160°	20	50	30
2. From needles and twigs of *Abies alba* (Miller) (*Abies pectinata*; silver fir).	0.869 to 0.875 0.885	−20 to −59 −35	1 : 5 1 : 6.5	4.5 to 11 6.1	162°	8	55 55 (Limonene.)	37
3. From cones of *Abies alba* (Miller) (fir-cone oil).	0.853 to 0.870	−60 to −76	1 : 6	0.5 to 4	....	11	37 (Limonene.)	52
4. From twigs of *Abies alba* (*A. pectinata*).	0.854	−72.4	....	(No borneol.)	....	16	76	8
5. Needles and young twigs of *Pinus pumilio* (Haenke) *Pinus Montana*).	0.865 to 0.875	−4.5 to −9	....	5 to 7	170°	....	70 (to 180)	30
6. Needles of *Pinus sylvestris* (English).	0.885 to 0.889	−7.7 to −19	....	2.9 to 3.5	....	8 to 13	33 to 47	....
7. Needles of *Pinus sylvestris* (German).	0.884 to 0.886	+7 to +10	1 : 10	3.2 to 3.5	160°	10	46	44
8. Needles of *Pinus sylvestris* (Swedish).	0.872	+10.7	....	3.5	160°	44	40	16
9. Needles of *Pinus cembra* (Siberian Cedar).	....	+29.1	....	....	....	....	....	....

CHARACTERS OF PINE-NEEDLE OILS.—CONTINUED.

	Sp. gr., 15.5°	Opt. rot.°	Solubility in alcohol (90%)	Esters as bornyl acetate. %	Behaviour on distillation			
					First distillate at	150 to 170°, %	170 to 185°, %	Residue, %
10. Needles and twigs of Abies Siberica (Siberian (Larix Siberica).	0.905 to 0.920	−40 to −42	1 : 1	35				
11. Needles of Picea nigra (black spruce).	0.922 (20°)	−36.4		48.8	(Chiefly at 212° to 230°.)			
12. Needles and young twigs of Abies Canadensis (hemlock); Picea alba (white spruce; and Picea nigra (mixed distillate) [hemlock or spruce oil].	0.907 to 0.913	−21 to −24		36		11	37	52
13. Fresh twigs and young cones of Balsam fir. (North America).	0.888 (20°)	−28.9		17.6		49	20	22
14. Needles of Larix decidua (Larch).	0.878	+0.7	1 : 5	8.1		54	24 (to 190°)	
Factitious Oil.								
A.	0.873	+14				96	1	3
B.	0.858	+4				95	1	4
C.		Inactive.				100		

lævopinene, the product of the ordinary fir contains the dextromodi-
fication.

According to Tröger and Bentin (*Arch. Pharm.*, 1904, **242,** 521),
the oils distilled from the young shoots of *P. sylvestris* and *P. strobus*
contain dextro- and lævopinene, respectively, but âre free from
sylvestrene, cadinene, and the borneol esters present in the oils from
older leaves, which compounds are thus produced in later growth.

Of the *factitious pine oils* represented in the table, A and B consisted
substantially of ordinary turpentine oil with a small addition of true
pine-needle oil, while C contained ethyl acetate which distilled as a
first running below 150°.

In a fraction of Siberian pine-needle oil, b. p. 240° to 280°, Wallach
and Grosse (*Ann.*, 1909, **368,** 19) found a sesquiterpene which readily
yielded a crystallizable hydrochloride.

Rose Oil (Otto of Roses; Attar of Roses).

This essential oil, so important to the perfumer, is obtained from
the fresh flowers of *Rosa Damascena, R. centifolia, R. alba*, and other
varieties and is chiefly distilled in Bulgaria. The oil is very liable
to adulteration, and both the Bulgarian distillers and the Turkish
dealers sometimes add palmarosa oil (Turkish geranium) and other
products. An examination of the "odour" of rose otto is still one of
the best guides to purity.

Rose oil deposits at ordinary temperatures a variable amount of
stearoptene as a crystalline mass. The white rose yields a somewhat
larger quantity of stearoptene than the red rose. At temperatures
slightly higher (20°), rose oil is a pale yellow fluid. Its sp. gr. at 15.5°
is 0.860 to 0.870, and about 0.848 to 0.858 at 30° (rarely above
0.856). The British Pharmacopœia (1898) states that rose oil
(which according to that authority should be distilled from *R. Dama-
scena*) has a sp. gr. of 0.856 to 0.860 at 30°, and congeals and melts
at from 19.4° to 22.2°. These requirements are misleading and
inadequate. The congealing and m. p. of the oil differ according to
the proportion of stearoptene present.

Rose oil is only slightly optically active, the mean rotation being
about −3°. Some few German oils are faintly dextrorotatory (+1°).

Citronellol from oil of roses is, however, lævorotatory to the extent
of −4.3°.

According to Parry (*Chemistry of the Essential Oils*, 2d Ed.), the ref. index is a valuable datum, and should fall within the limits 1.4580 and 1.4650. Geraniol raises this figure perceptibly, so does palmarosa oil, which has a ref. index of 1.4745. Alcohol has ref. index 1.365.

The *constituents of rose* oil have been the subject of much study. It has been known for many years that rose oil and oils of the geranium variety contain an alcohol, $C_{10}H_{18}O$, to which Jacobsen in 1870 gave the name "geraniol." Bertram and Gildemeister then recognised that rose oil contained a mixture of 2 alcohols, of which geraniol, $C_{10}H_{18}O$, was the chief. Tiemann and Schmidt finally proved the identity of the other alcohol with that obtained by Dodge in 1890 by reduction of citronell-aldehyde. This alcohol is citronellol, $C_{10}H_{20}O$. Much confusion has arisen on account of the numerous names which have been given by the various workers on the subject to one or other of these 2 alcohols. Many of these names have now been abandoned, as most of the products have been found to consist of geraniol and citronellol in varying proportions. Thus the "rhodinol" of Erdmann and Huth, and the "lemonol" of Barbier and Bouveault consist of geraniol; the "rhodinol" of Eckart, the "roseol" of Marknovnikoff and Reformatsky, and the "réuniol" of Hesse are mixtures of geraniol and citronellol; whilst the "rhodinol" of Barbier and Bouveault and the "réuniol" of Naschold are identical with citronellol. Substances sold in commerce under the names of "rhodinol" and "réuniol" are mixtures of geraniol and citronellol.

Commercial "rhodinol" consists of a mixture of 30 to 40% of citronellol and 60 to 70% of geraniol. "Licarhodol" was the name given by Barbier to a product obtained by heating linalol with acetic anhydride. According to Schimmel & Co., it consists of geraniol and dextroterpineol.

The principal constituents of both Bulgarian and German oil of roses are, therefore, the alcohols geraniol and citronellol. These alcohols are present in the oil in the proportion of 75% of geraniol to 25% of citronellol. German oils, however, contain less citronellol than Bulgarian oils.

The presence of geraniol in oil of roses (and also in African geranium oil) may be shown by treating the liquid portion of the oil with calcium chloride, when the characteristic crystalline geraniol-calcium chloride compound is produced. Citronellol does not form a corresponding compound. Another method of detecting the

presence of geraniol in essential oils is to isolate the diphenylurethane
derivative which crystallises in colourless needles, m. p. 82°. Cit-
ronellol diphenylurethane is an oily, non-volatile body. Citronellol
is determined in rose oil by formulating a mixture of 1 volume of oil
with 2 vols. of 100% formic acid, heating for 1 hour over a reflux
condenser. The method is then conducted as in the acetylation of oils
(page 227). Other processes for the detection and estimation of the
open-chain alcohols in rose oil, are described in detail on page 227
et seq.

In addition to the 2 chief alcoholic constituents and the stearoptene,
already described, other substances occur that, although in small
quantity, appreciably modify the odour. Among these are traces of
esters of geraniol and citronellol together with acids produced by slight
decomposition. According to some observers an easily hydrolysed
lævorotatory ester is present in the oil, and to the decomposition of
this is ascribed the acidity of rose-flower water. Walbaum and
Stephan have proved the presence of normal nonyl aldehyde, citral,
and linalol. Schimmel & Co. prepare a synthetic "otto" based on
the researches of Walbaum and Stephan. Erdmann has shown normal
phenyl-ethyl alcohol to be present (partly as esters) and, according to
Eckart, ethyl alcohol (5% of the liquid portion) is a normal constituent
of the oil, but this is only present in the product from roses which have
partially fermented before distillation (Poleck). Von Soden and Treff
claim to have isolated nerol (5 to 10%), eugenol (1%), and a
sesquiterpene alcohol ("farnesol"?), 1%. Phenyl-ethyl alcohol is
especially important as contributing to the odour of rose otto, but,
although this compound is present to a considerable extent in rose-
flowers, it only occurs in small amount in rose otto, being largely lost
in the distillation-water.

The *stearoptene* present in rose oil is apparently a mixture of 2 solid
hydrocarbons, m. p. 22° and 41°, respectively. The mixed substance
as it exists in the oil melts at 33° to 35°. The proportion of stearop-
tene present in different oils varies within very wide limits, so that the
amount of this constituent is no criterion as to the purity of the oil.
According to E. J. Parry, Bulgarian oils contain 10 to 20% of stearop-
tene, while the oils from France, Germany, and England are said to
contain 25 to 60%. Any oil containing a percentage of stearoptene,
even approaching this higher figure, cannot be regarded as a normal
product.

The sp. gr. of rose oil ranges between fairly wide limits and according to the proportion of stearoptene. Adulteration of rose otto with alcohol causes a low sp. gr., of about 1.4745.

The congealing-point (setting-point) of rose otto may be ascertained in the following manner (P. N. Raikow, Chem. Zeit., 1898, 22, 149): About 10 c.c. of the oil to be examined is placed in a test-tube of 15 mm. diameter, and the oil warmed by means of the hand until it attains a temperature well above the solidifying-point. A thermometer is meanwhile placed in the oil in such a manner that it touches neither the bottom nor sides of the tube, but has its bulb completely immersed. The oil is allowed to cool spontaneously, and the temperature at which the first crystals appear is the congealing-point. Duplicate determinations should be made. This method has been adopted in the United States Pharmacopœia (8th Rev.), which requires rose oil to congeal at a temperature between 18° and 22°.

The United States Pharmacopœia further requires rose oil to have a sp. gr. of 0.855 to 0.865 at 25°, and to show a saponification value of not less than 10 nor more than 17 when treated by the usual Koettstorfer's process (see Vol. 1), about 2 c.c. of the oil, accurately weighed, being used for the determination. The number of c.c. of $N/2$ alcoholic potassium hydroxide absorbed by the oil in the process, multiplied by 27.87 and divided by the weight of oil taken, gives the saponification-value of the oil.

Adulterated rose oil may contain paraffin-wax or spermaceti, which should be looked for in the separated solid portion of the oil. The stearoptene of rose oil usually melts at 33° to 34°, and should not exceed the limits of 32° to 37°. Higher m. p. indicate adulteration with paraffin-wax or spermaceti.

Parry states (Chemistry of Essential Oils) that while the detection of spermaceti and stearin in rose oil is comparatively easy, the detection of paraffin-wax or the solid constituent of "guaiacum-wood" oil presents greater difficulty. On saponifying the stearoptene of the oil under examination, no fatty acids will be obtained if the oil is pure, while spermaceti and stearin yield palmitic and stearic acids (m. p. at 55°-62° and 62°-68°, respectively). Paraffin-wax may be detected by its more granular crystalline structure as compared with the rose stearoptene. The alcoholic body from guaiacum-wood oil will yield an acetyl-number. Antipyrin is occasionally found as an adulterant of rose-otto.

According to E. P. Paetzold, the so-called concrete oil of guaiacum-wood is the product of *Bulnesia sarmienti*, and is one of the chief adulterants of Turkish rose oil. It is used especially in conjunction with geranium oil. It has a mild tea-like odour, and consists largely of a crystalline alcohol of m. p. 91°, and is thus semi-solid at the ordinary temperature. The oil is stated to have a sp. gr. of c.969 at 35° and an opt. rot. of —6.7°.

The following figures show the physical characters of different varieties of rose oil, as recorded by various observers:

Variety of rose oil	Observers	Sp. gr.	Opt. rot., °	Solidifying pt.	Stearoptene, %
	Brit. Pharm., 1988	0.856 to 0.860 (30°)	....	19.4 to 22.2	....
	U. S. Pharm.	0.855 to 0.865 (25°)	....	18 to 22	....
Bulgarian.	Dupont and Gueslau	0.865 (30°)	—3.5	....	6 to 13
Bulgarian.	J. C. Umney	0.856 to 0.860 (30°)	....	20 to 21	16 to 18
Bulgarian.	M. Conroy	0.850 to 0.856 (30°)	—2.3 to —2.7	....	....
Bulgarian.	E. J. Parry	0.848 to 0.858 (30°)	—1.8 to —4.0	17 to 23	18 to 22.5
French....	Schimmel & Co.	....	—7 to —9	....	....
French....	Dupont and Gueslau	{ 0.8225 (30°) { 0.8407 (30°)	—6.8 —8.05	....	35 26
German...	P. N. Raikow	0.853; 0.858 (27.5°).	—2.7; —2.1	20.5; 22.5	....
German...	Schimmel & Co.	0.837; 0.830	—0.75	29; 30	28.5; 40
Persian....	Schimmel & Co.	0.832 (25°)	—9.1	21.5	....
Russian...	Bertrand Fils	0.836 (30°)	—4.2	23	33.5

Parry (*Chem. and Drug.*, 1909, **75,** 186) examined four authentic samples of the crop of 1909 and found the following range of constants:

Sp. gr. 30°, 0.8568 to 0.8573;

Opt. rot. —2° 30′ to —3°;

Ind. ref. 25° 1.4626 to 1.4730.

After washing with water the ref. ind. was 1.4630 to 1.4638; m. p., 22.5°. Total geraniol, 68.5 to 71%.

The sp. gr. of rose oil is not of much value when considered apart from other constants, since the several varieties of the oil differ to a not inconsiderable extent, and the content of stearoptene also causes differences. According to J. C. Umney, a rose oil having a sp. gr. exceeding 0.861 at 30° should be looked upon with suspicion. The figures for the opt. rot. of rose oil and its adulterants do not show sufficiently well-marked differences to be valuable in determining the purity of rose oils.

The m. p. and solidifying-points of genuine rose oils may be taken as lying between the limits 17° and 23°, although the percentage of

stearoptene affects them. A high solidifying-point indicates excess of stearoptene (or adulteration with paraffin-wax), while the odour of the oil will be correspondingly weakened. Oils adulterated with geranium oil have a lowered solidifying-point and of course contain a decreased proportion of stearoptene. For the estimation of the amount of stearoptene present in the oil, Schimmel & Co. (*Rep.*, 1889) advise to heat 50 grm. of the sample with 500 grm. of 75% alcohol to 70° to 80°. On cooling the mixture to 0° the stearoptene separates almost quantitatively. The liquid is filtered, again treated similarly with 200 grm. of the alcohol, and this treatment is continued until the stearoptene is quite odourless. 2 treatments of the crude stearoptene are usually sufficient, and the product is then dried and weighed.

According to F. Dietze, the acid and ester numbers of pure rose oils (in terms of % potassium hydroxide) range from 0.12 to 0.26 (acid number) and from 0.65 to 1.9 (ester number), while geranium oils show an ester number of 2.6 to 7.2. These constants are of very doubtful value as an indication of purity (see P. N. Raikow, *Chem. Zeit.*, 1898, **22**, 149).

The estimation of the alcoholic constituents of rose oil (by the acety-lation process, page 227) would appear to be of some value as a criterion of purity, in spite of many statements to the contrary. Umney found the finest ottos to contain 71 to 72.5% of total alcohols. High stearop-tene-content lowers this figure, while admixture with geranium oil raises it considerably, and at the same time increases the sp. gr. Um-ney cites the following results (among others) obtained by the examina-tion of the genuine and adulterated samples of rose oils:

	Genuine oils			Adulterated samples		
	1	2	3	4	5	6
Sp. gr., 30°	0.875	0.860	0.861	0.863	0.868	0.808
Crystallising-point	20.9	20.4	20.0	19.4	18.7	18.9
Stearoptene, %	18	16	14	12.5	10	10
Alcohols (as $C_{10}H_{18}O$)	70.1	72.3	73.1	75.6	77.6	76.6

Hudson-Cox and Simmons (*Analyst*, 1904, **29**, 175) recommend the iodine-absorption figure as a means for detecting adulteration of natural otto of rose with the synthetic product and other substances. These observers employ 0.1 to 0.2 grm. of otto, adding 10 c.c. of chloro-form or alcohol (90 %), and 25 c.c. of Hübl's iodine solution. The

CHARACTERS OF GENUINE AND ARTIFICIAL ROSE OTTOS.

	Sp. gr. at 30°	Opt. rot., 30°	Sapon. number	Solidifying pt.	Iodine absorption, %	Remarks
Genuine ottos (5 samples)......	0.851 to 0.859	−2.11 to −2.7	7.5 to 15.5	20.3 to 21.0	187 to 194	....
Genuine ottos (5 samples)......	0.852 to 0.856	−1.8 to −3.2	7.7 to 9.9	19.9 to 21.6	189 to 192	Refractive indices, 1.4613 to 1.4646.
Artificial Ottos.						
With stearoptene (2 samples)...	0.863; 0.859	−0.9; −0.2	20.5; 3.8	22.5; 21.9	(221 to 254)	
Without stearoptene (2 samples)	0.872; 0.866	−1.3; −0.9	13.4; 5.7	....	(261 to 279)	
Commercial Ottos.						
No. 1...............	0.855	−2.7	8.9	20.8	219	Probably contained geraniol.
No. 3...............	0.855	−2.7	8.1	19.8	206	Probably contained artificial otto.
No. 4...............	0.858	−1.4	10.3	21.3	234	Chiefly artificial otto.
No. 6...............	0.843	−0.8	16.1	18.5	133	Contained much added alcohol.
No. 8...............	0.855	−2.0	9.8	20.6	215	Mixture of 1 part artificial with 2 parts of genuine otto.

excess of iodine in the mixture is titrated in the usual manner after
the liquid has been allowed to stand for 3 hours in the dark at the
ordinary temperature. Considerable differences in temperature
have no appreciable effects on the results. Hudson-Cox and Simmons
use only Hübl's solution of full strength, and consider it convenient and
advisable to keep the iodine and mercuric chloride solutions sepa-
rate, and mix them the evening before using. The titration should be
carried out as rapidly as possible. It is noteworthy that while the arti-
ficial otto is almost deodorised by iodine, the natural otto is unaffected
in this respect. The following results, in addition of those recorded in
the table below, were obtained in this manner: Palmarosa oil, 296 to
307% of iodine absorbed; geranium oils: (African), 213 to 225,
(Bourbon), 213 to 215, (Spanish), 211; citronella oil, 217; guaiacum-
wood oil, 298; geraniol, 307 (?); citronellol 187; linalol, 280; citral,
175; and the stearoptene of rose oil, none. With the exception of
citronellol and citral, all the iodine values largely exceed those of
genuine otto of rose, the oils of citronella, which most closely resemble
otto of rose in this respect, being readily recognisable by their ester-
content.

The figures in the table (page 388) have been recorded by Hudson-
Cox and Simmons and by W. H. Simmons (*Chem. and Drug.*, 1904,
65, 707) for various samples of genuine and artificial ottos and their
adulterants.

Jeancard and Satie (*Bull. Soc. Chim.*, [3], 1904, **31,** 934) found an oil
distilled from the calyx, stamen, and pistil of the rose to have the follow-
ing characters: Sp. gr. 0.8704 at 15.5°; optical rotation, 41°; solidi-
fying-point, 8°; acid number, 6.12; ester number, 22.4; stearoptene
(chiefly a substance melting at 14°) 51.1%; and citronellol (the only
alcohol present), 13.6%.

Schimmel & Co. (*Rep.*, Oct., 1909, 107) report a case of adultera-
tion of Bulgarian rose oil with both alcohol and geraniol. The only
irregularity observed was in the index of refraction, but on washing
the sample with water the sp. gr. at 30° was increased from 0.8606
to 0.8632, the ref. ind. from 1.4656 to 1.4667 and the congealing
point from 20° to 21°.

Rosemary Oil.

This oil is distilled from the flowering tops of *Rosmarinus officinalis*.
It is a pale yellow or colourless oil, having an odour of rosemary and

a warm camphoraceous taste.   The oil distilled from the dried leaves
without admixture of stalks is the finest product, having a good odour
and high borneol-content.

Oil of rosemary is official in the British and United States Pharmaco-
pœias.   It is described in the British Pharmacopœia (1898) as an oil
of sp. gr. o. 900 to o. 915, which dissolves in 2 volumes of 90% alcohol.
It should have an opt. rot. of not more than +10°.   The latter con-
stant guards against the presence of turpentine oil (see below).   The
United States Pharmacopœia requires rosemary oil to have an opt. rot.
of not more than +15°, and to give 10% fraction showing dextro-
rotation.   .

The constituents of oil of rosemary are somewhat numerous and
include camphor, cineol, borneol and its esters (chiefly bornyl acetate),
and traces of dextropinene and camphene.   Haller (C. r., 1889, 108,
1308) states that both dextro- and lævocamphor and dextro- and
lævoborneol are present in oil of rosemary.

English oil of rosemary is more valued in commerce than either the
French or the so-called Italian variety.   The latter is the cheapest oil.
It is actually produced in certain of the Dalmatian Islands.

The sp. gr. of genuine oil of rosemary (English and foreign) varies
from o.900 to o.918, possibly occasionally to o.920, and thus the
Pharmacopœial limits are somewhat too narrow.   The sp. gr. is
altered by the addition of oil of turpentine, with which rosemary oil
is sometimes adulterated.   Parry regards the limits o. 896 to o. 920 as
covering all genuine oils.

Schimmel & Co. (Rep., 1900) state that Spanish oil of rosemary
has a higher sp. gr. and greater optical activity than other kinds.   A
sample of this oil, examined by them and stated to be absolutely pure,
was found to have a sp. gr. of o.932; optical rotation, +17.5 at 20°;
optical rotation of first 10% distilled, +4.75 at 20°.   The oil was
soluble in 2 vols. of 80% alcohol.

The optical rotation only rarely exceeds +10°, the British Phar-
macopœia limit; Parry gives +1° to +12°.   Dalmatian oils usually
give figures between the limits of +1° to +4°.   Spike oil is sometimes
added to oil of rosemary, and this adulterant does not interfere with
the sp. gr. of opt. rot.   It has recently been pointed out by Parry and
Bennett that lævorotatory oils of rosemary are quite consistent with
purity.   These observers have found that the herb from Spanish and
French sources may yield oils having either a lævorotation (−3°;

−8.5°) or giving a lævorotatory first fraction (10%) on distillation (100 mm. pressure). These results are due to the lævopinene present naturally in the rosemary stems. (See *Chem. and Drug.*, 1906, **68**, 671.)

Genuine oil of rosemary should be soluble in from 0.5 to 2 vols. of 90% alcohol, and in 2 to 10 volumes of 80% alcohol. The solubility of rosemary oil in alcohol is disturbed by adulteration with turpentine oil or the higher fractions of petroleum.

Rosemary oil is occasionally adulterated with alcohol, which may be detected by fractional distillation. Genuine oils do not give more than about 15 to 20% of distillate under 170° (at the ordinary pressure). A larger amount than this indicates the presence of alcohol or turpentine oil. The greater portion of rosemary oil distils between 175° and 200°.

The higher fractions of petroleum oil which are sometimes used as adulterants of rosemary oil may be detected by evaporating a sample of the oil upon the water-bath, a slight residue only remaining if the oil is genuine while any petroleum oil will remain unvolatilized.

The proportions of esters and free alcohols are determined in the usual way (page 227). Calculated as borneol and bornyl acetate, the percentage of these constituents in genuine rosemary oils averages about 17 to 18% of alcohols, and 5 to 6% of esters. The proportions of these constituents appear to range between fairly wide limits. The lowest allowable limit for ester content might be placed at 4.5 to 5% (calculated as bornyl acetate), while 10% of alcohols (calculated as borneol) should be regarded as the lowest amount allowable, and probably 12% would be a fairer limit. Many oils contain considerably more alcohols than this, as stated in the text. Umney found 3 genuine oils to contain from 11 to 15% of alcohols.

The United States Pharmacopœia (8th Rev.) requires the oil to contain at least 5% of esters (as bornyl acetate) and at least 15% of total borneol.

Sandalwood Oil (Santalwood Oil).

There are many varieties of this oil, as several plants of the natural order *Santalaceæ* are used for its distillation. The most valuable oil, which is official in the British and United States Pharmacopœias, is from the East India sandalwood, *Santalum album*. The other chief commercial varieties are Macassar and West Australian. Less im-

portant are the West Indian and African oils. The East Indian and Macassar oils are derived from *Santalum album;* the Australian variety is often the product of several plants; the oil known as Swan River oil being obtained from *S. cygnorum.*

Sandalwood oil is somewhat viscid, pale yellow, with a character-istic odour and a spicy taste. The British Pharmacopœia requires it to have a sp. gr. between 0.975 and 0.980, and to be soluble in 6 volumes of 70% alcohol (United States Pharmacopœia, soluble in 5 vols.). This latter test ensures the absence of cedar-wood oil, and possibly other adulterants. The oil should have an optical rotation (according to the British and United States Pharmacopœias) of from −16° to −20°. These limits of optical activity are so arranged as to exclude any other variety of oil than the product of *S. album.* The United States Pharmacopœia gives the limits of sp. gr. as 0.965 to 0.975 at 25°.

The sp. gr. of the official (East Indian) sandalwood oil is usually slightly higher than the other oils of sandalwood. Parry states that he has found genuine samples to range from 0.973 to 0.981. The higher limit of the British Pharmacopœia (0.980) might perhaps with advantage be raised to 0.985, as in the German Pharmacopœia. It has been pointed out that the sp. gr. of sandalwood oil continually increases from the commencement of the distillation to the end, so that it is necessary to take the distillation as far as possible. Thus Parry found that the sp. gr. of the oil in the first, middle, and last portions of the distillate was 0.965, 0.976, and 0.981, respectively.

Oil of sandalwood differs to an appreciable extent according to the character of the wood used in distillation. Oils from billets and roots have the finest aroma and are most used in perfumery; while oils from chips contain most santalol and are the best for pharmaceutical use.

The pharmacopœial limits for optical rotation are rarely exceeded. All genuine oils give figures between −15° and −20°, and usually between −17° and −19°. Most samples of genuine sandalwood oil are soluble in 4 to 4.5 parts of 70% alcohol at 20°.

Oil of sandalwood distils (at ordinary atmospheric pressure) between 275° and 295°, with decomposition. The results obtained by distillation under a reduced pressure of 14 mm. are much more valuable for the detection of adulteration, as it distils between 155° and 170°, but cedar-wood oil, a frequent adulterant, distils largely

below 150° under the same conditions. According to Parry and Bennett (*Chem. and Drug.*, 1904, **64,** 202) the genuine oil (East Indian) when distilled under this reduced pressure and the distillate collected in 10% fractions, gives the following results: The sp. gr. of the fractions varies from 0.964 to 0.988; the optical rotation from —14° to —22°; and the ref. index from 1.5038 to 1.5123. No fraction should have a ref. index below 1.5000, and the opt. rot. of the fractions should range only within narrow limits when thus distilled. The ref. index of 8 genuine samples was found by Parry and Bennett to range from 1.5040 to 1.5075 (usually about 1.5060). This figure should never be below 1.5030.

The United States Pharmacopœia contains the following test for the detection of chloroform in adulterated oils: Fold a small strip of filter-paper into the form of a taper, saturate it with sandalwood oil, ignite the oil on the taper, and absorb the soluble portions of the products of combustion by holding over the flame an inverted beaker moistened on the inside with distilled water. The presence of a chloride in the water after the test is completed is evidence of the presence of chlorinated products (such as chloroform) in the original oil.

The composition of sandalwood oil has for a long time been the subject of research, since the chemistry of the alcoholic bodies present (forming about 94 to 98% of the oil) was until recently in a very confused state. The subject is by no means fully cleared up, but it seems certain now that the so-called "santalol" is a mixture of *at least* 2 alcohols (isomeric?), termed α- and β-santalols, of which the former is present in the larger quantity and is probably slightly dextrorotatory, the latter being a strongly lævorotatory compound (about —45°). Many authorities doubt the accuracy of the formula $C_{15}H_{25}.OH$ for "santalol"; thus Schimmel & Co. consider that it is either a mixture of isomeric alcohols of the formula $C_{15}H_{21}.OH$, or consists of non-isomeric alcohols. Other formulæ have been suggested (*e. g.*, $C_{15}H_{24}O$), but the constituent alcohols have not yet been isolated in a pure state. It is possible that a third alcohol may be present in the "santalol" mixture.

In addition to the 2 or more alcohols ("santalol"), sandalwood oil contains a small proportion of esters of these or other unidentified alcohols; santalal, $C_{15}H_{24}O$, 3%; α- and β-santalenes, 6% (b. p., 253° and 263°, respectively); traces of acetic and formic acid; teresan-

talic acid, $C_{10}H_{14}O_2$; santalic acid, $C_{15}H_{24}O_2$ (total acids about 3%, mostly as esters); and, according to Müller, a compound, C_9H_{14} ("santene"), a lower homologue of the terpenes, and santalone, $C_{11}H_{16}O$ (isomeric with jasmone). The odorous substances (b. p., 210° to 220°) of the oil have not yet been identified, unless the ketone santalone be one of them.

Oxidising agents, as for example potassium permanganate, act upon sandalwood oil with the formation of a crystalline acid, termed by Chapman *santalenic acid*. It is possible that further investigations as to the constitution of this acid may throw some new light on the constitution of the sandal alcohols.

The acetylation process was first applied by Parry (*Pharm. J.* [4], 1895, **1**, 118) to the examination of oil of sandalwood. It is carried out as described on page 227. Pure oils require from 0.7 to 1.5% potassium hydroxide for the saponification of the esters; but after acetylation the oil takes up 20 to 21%, owing to the presence of the large proportion of alcohols. Calculated as $C_{15}H_{26}O$, the proportion of alcoholic constituents should never fall below 90%, and a standard somewhat higher than this, say 92.5%, as suggested by Potoliet (*Brit. and Col. Drug.*, 1901, **40**, 173), would be preferable. The United States Pharmacopœia (8th Rev.), in which this method of valuation is now adopted, requires at least 90% of alcohols as "santalol." The usefulness of the acetylation method as a means of detecting adulteration may be seen from the following figures given by various oils used as adulterants, in comparison with pure sandalwood oil:

Oil, etc.	Alcohol by acetylation (Calculated as santalol, $C_{15}H_{25}OH$), %
Sandalwood, East Indian	92 to 98
Sandalwood, West Australian	about 75
Cedar-wood	8 to 12
Gurjun balsam	7 to 10
Copaiba balsam	5 to 8

The above-mentioned adulterants, together with castor oil, are those usually found in sandalwood oil. The last-named may be identified by the lowered sp. gr. and high saponification number. Parry has recently recorded the adulteration of sandalwood oil with the soluble fractions of West Indian oil together with terpineol, the

latter compound serving to give a fictitious santalol value. The sp.
gr. of these adulterated oils was slightly low, while the opt. rot. was
also decreased in some cases (—14°). (*Chem. and Drug.*, 1906, **68,**
211.)   •

The iodine absorptions of 5 samples of sandalwood oil of undoubted
purity were found by Parry to vary from 190.6 to 210.3. Higher
results (up to 264) were obtained by Pearmain and Moor. Similar
figures are given by cedar-wood oil and the method does not, therefore,
appear to be of much value as a test of purity.

A large proportion of the sandalwood oil used in medicine is put
up in the form of capsules. The oil in these capsules is frequently
grossly adulterated or is of an inferior quality. Many have been found
to contain cedar-wood oil, or one of the non-official sandalwood oils
(*e. g.*, West Indian). Parry has called attention to the grossly adulter-
ated capsules now on the market, many specimens consisting largely
of West Indian oil. Since it is the "santalol" of these oils which is of
medicinal value, the percentage of this mixture of constituents should
always be determined. Further, it should be borne in mind that
small quantities of West Indian sandalwood and cedar-wood oils
(about 4% of each) may be added to East Indian sandalwood oil
(see Potoliet, *Brit. and Col. Drug.*, 1901, **40,** 173) without any appre-
ciable departure from the physical and chemical characters of genuine
official sandalwood oil.

West Australian sandalwood oil is chiefly the product of
Santalum cygnorum, although certain other trees are said to be em-
ployed to a small extent. The sp. gr. of this oil is lower than that of
the East Indian variety, being about 0.950 to 0.965 at 15°. It is
usually slightly dextrorotatory, about 5°. Parry (*Chem. and Drug.*,
1898, **53,** 708) has recorded the results of the analysis of 4 samples
of this oil. They contained on the average 75.7% of "santalol"
(by acetylisation). Parry believes, however, that other reactions
occur during the process, and hence the above figure probably does
not represent the true amount of sesquiterpene alcohols present in
the oils.

The iodine absorption of these four samples of West Australian
oil was found by Parry to range from 197.6 to 204.5%. The alkali
absorbed ranged from 1.15 to 1.66%. The chief characters of the
less important varieties of sandalwood oil are shown in the follow-
ing table:

Variety of oil	Botanical source	Sp. gr. at 15°	Opt. rot.	Constituents and characters
West Indian....	*Amyris balsamifera (Schimmelia) oleifera).*	0.955 to 0.965	25° to 30°	30 to 40% of alcohol as "santalol," C_{15}-$H_{26}O$; 16% cadinene and other sesquiterpenes.
African........	Unknown.	0.969	....	Similar to West Indian oil.
South Australian	*Santalum preissianum.*	1.022	....	Solidifies on cooling; contains a solid alcoholic body, m. p. 101 to 102°.
Fiji...........	*S. yasi.*	0.9768	$-25.8°$	....
Macassar.......	*S. album.*	0.974 to 0.976	$-10.6°$ to $-16.1°$	Sol. in 5 to 6 pts. 70% alcohol; 88 to 92.5% "santalol."

West Indian oil is characterised by its insolubility in 70% alcohol, most samples of the oil requiring over 80 parts for solution. As seen from the table, it is not a true sandalwood oil. Von Soden has isolated from this variety of oil a sesquiterpene alcohol (or mixture of isomeric alcohols), termed by him "amyrol," $C_{15}H_{26}O$. Amyrol boils at 299° to 301°, and is soluble in 3 to 3.5 parts of 70% alcohol at 20°. A compound termed *amyrolin*, $C_{24}H_{42}O_3$, is also present (Von Soden and Rojahn, *Pharm. Zeitung.*, 1900, **45**, 878.

Sassafras Oil.

Sassafras oil, which is of great commercial importance in the United States on account of its use as a perfume in cheap toilet soaps, is obtained from the bark of the root of *Sassafras variifolium* (*S. officinale* or *S. sassafras*) a tree indigenous to North America. While the bark of the root contains the major portion of the oil, the wood contains a small amount, and the usual custom is to use the whole root.

The physical properties, as given by the United States Pharmacopœia, are as follows: Yellow or reddish-yellow liquid, having the characteristic odours of sassafras and a warm aromatic taste, sp. gr. 1.065 to 1.075 at 25°. The oil is dextrorotatory, but should not show more than $+4°$ at 25°. Soluble in all proportions in 90% alcohol, the solution being neutral to litmus-paper." The ref. index is about 1.5275. The oil contains about 80 to 90% of safrol together with small amounts of pinene, phellandrene, dextrocamphor, eugenol, and cadinene. It is being largely replaced in soap perfumery by the safrol obtained in *fractionating camphor oil*. The oil of sassafras leaves and stem bark

is totally different from the foregoing in its physical and chemical properties.

Snake-root Oils (Oils of Asarum Europæum and Asarum Canadense).

These 2 oils are the products of the distillation of the rhizomes and roots of *A. Europæum* and *A. Canadense*, respectively. The chief known characters of the different snake-root oils are contained in the following table:

Oil	Source	Sp. gr. at 15.5°	Other characters and constituents
European snake-root	Rhizome and root.	1.015 to 1.070	Brown, aromatic. On long standing, the oil is said to deposit crystals of asarone. Contains lævopinene; methyl-eugenol or -isoeugenol, and a blue-green high-boiling fraction.
Canada snake-root	Rhizome and root.	0.930 to 0.960	Yellow or yellowish-brown oil of strong aromatic odour. Optical rotation, $-3.5°$. Contains d- and l-pinenes (2%); d-linalol; d-borneol; l-terpineol; geraniol (total alcohols, 35%); methyl-eugenol (37%); a phenol, $C_9H_{12}O_2$; a lactone, $C_{14}H_{20}O_2$; a mixture of fatty acids, including acetic and palmitic; a blue oil, consisting of oxygenated bodies of an alcoholic nature (about 20%).
Virginia snake-root	Whole herb of *Aristolochia serpentaria*.	0.980 to 0.990	Contains an ester of borneol.
. . . .	Root of *A. reticulata*.	0.974 to 0.978	Optical rotation, $= -4°$; contains pinene and borneol.
. . . .	Root of *A. clematis*.	About 0.910	A thick yellow oil.
. . . .	Dried herb of *Asarum arifolium*.	1.0585 to 1.0613	Optical rotation, $-2.5°$ to $-3.7°$. Contains safrol (chief constituent); lævopinene; eugenol; a phenol; methyl-eugenol and methyl-isoeugenol; asarone, and a sequiterpene.

It would appear that a further investigation of the composition of some of the oils is desirable, although they are not of any great importance. Our present knowledge of them, as given in the above table, is chiefly due to the researches of F. B. Power (*Proc. Amer. Pharm. Assoc.*, 1880, **28**, 464); Petersen (*Arch. Pharm.*, 1888, **226**, 123) and Power and Lees (*J. Chem. Soc.*, 1902, **81**, 59).

Thyme Oil.

This oil is obtained by the distillation of *Thymus vulgaris*, and is produced largely in Spain and France. The Spanish oil is the more valuable. In the south of France the oil not infrequently suffers

admixture with the oil of *Thymus serpyllum* and with French oil of turpentine.

2 varieties of oil of thyme, namely the "red" and "white," are known in commerce. The name usually applied in pharmacy to oil of thyme which is frequently used in liniments especially by veterinary practitioners is oil of origanum. True oil of origanum·is of different physical and chemical properties, and is obtained from *Origanum vulgare*, *O. hirtum*, and *O. Smyrnæum*. The unrectified ("red") oil is stated to owe its colour to the action of the phenolic constituents of the oil on the iron of the apparatus employed in the distillation. The oil can be rectified to a light yellow-coloured oil ("white oil of thyme"). The sp. gr. of thyme oil ranges from about 0.905 to 0.950. It is slightly lævorotatory, to $-3°$ for 100 mm. Parry gives the ref. index as 1.4800. It is soluble in half its volume of 90% alcohol, in 1 to 2 volumes of 80%, whilst with from 15 to 30 volumes of 70% alcohol most genuine thyme oils afford a clear solution.

The constituents, so far as known, are the phenols thymol and carvacrol; the alcohols linalol and borneol; bornyl acetate; menthene (15%); cymene, and (possibly) lævopinene.

Thymol and carvacrol do not appear to be constantly present together in thyme oil. The conditions under which one or other of these isomeric phenols is present are not definitely known. Schimmel & Co. found that the oil from dried French thyme contained much thymol, but only a little carvacrol. French and dry thyme (German) gave oils containing only thymol. Spanish thyme oil was found to contain carvacrol and no thymol.

H. Labbé (*Bull. Soc. Chim.* [3], 1898, **19**, 1009) could not obtain any evidence of the presence of pinene in this oil, although he isolated a hydrocarbon boiling at 156° to 158°, which gave a nitroso-chloride, m. p. 106.5°. Labbé suggests that the oil examined by Schimmel & Co. and found to contain pinene was adulterated with oil of turpentine.

The *phenolic constituents* of thyme oil are perhaps the most important, although there is no doubt that the borneol and linalol contribute to the odour of the oil. The percentage of thymol and carvacrol in thyme oil is usually about 20 to 30, and should never fall below 20%. The phenols may be estimated approximately by noting the proportion dissolved out by sodium hydroxide solution, or by observing the amount of distillate obtained above 220°. This should not be less than 25% of the oil.

The United States Pharmacopœia (8th Rev.) requires thyme oil to contain at least 20% by volume of phenols, the oil being assayed by shaking 10 c.c. of the sample in a corked burette with 20 c.c. of 5% sodium hydroxide solution, and setting the mixture aside for 12 to 24 hours. The volume of unabsorbed (non-phenol) oil is then noted, and the proportion of phenols deduced.

The following method for the estimation of the phenols in thyme oil is due to Kremers and Schreiner (*Pharm. Rev.*, 1896, **14,** 221). The method is in reality a modification of that of Messinger and Vortmann (*Ber.*, 1890, **23,** 2753).

5 c.c. of the oil to be examined is weighed and introduced into a burette. The oil is diluted with about an equal vol. of petroleum spirit, when a 5% solution of potassium hydroxide is added and the mixture vigorously shaken for a short time. The liquid is then allowed to stand until separation is complete. The alkaline solution is now run off into a 100 c.c. flask. The agitation with the alkali is repeated until no further diminution of the volume of the oil occurs.

The alkaline liquid containing the dissolved thymol is now made up to a definite volume (100 or 200 c.c.) with 5% potassium hydroxide solution. An aliquot portion of this liquid (say 10 c.c.) is now introduced into a 500 c.c. flask, and $N/10$ iodine solution added in slight excess. In order to determine whether an excess of iodine has been added, a few drops of the liquid in a test-tube should be treated with a little dilute hydrochloric acid. If insufficient iodine has been added, the liquid will become milky owing to the separation of thymol. In the presence of an excess of iodine, a brown colour only will be seen. The thymol combines with the iodine, and a reddish-brown precipitate is produced. When excess of iodine has been added, the liquid is rendered slightly acid with dilute hydrochloric acid, and diluted to 500 c.c. with water. $1/5$ of the liquid (100 c.c.) is now filtered off, and titrated with $N/10$ sodium thiosulphate solution. Each c.c. of $N/10$ iodine solution is equivalent to 0.003741 grm. of thymol, the reaction which occurs being represented by the following equation:

$$C_{10}H_{14}O + 2I_2 + 2NaOH = C_{10}H_{12}I_2O + 2NaI + 2H_2O.$$
Thymol. Di-iodo-thymol.
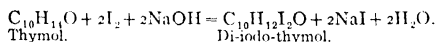
In the case of carvacrol, a finely divided white precipitate is produced with the iodine solution. The liquid is therefore vigorously shaken after the addition of the iodine solution and then filtered. The filtrate is next acidified with hydrochloric acid, and the process

continued exactly as the estimation of thymol. Since thymol and carvacrol are isomeric methyl-propyl phenols, and the same reaction occurs in both cases, the calculation in the case of the latter is the same as for thymol.

"White" French thyme oil is said to be almost invariably of poor quality and, as has been stated, is frequently adulterated with French oil of turpentine. Such adulterated oils would be strongly lævorotatory. The addition of the oil from *Thymus serpyllum* (wild thyme) to genuine thyme oil also increases the rotation (see table on next page).

The abstraction of thymol from thyme oil is much practised, and it is therefore important to determine, at least approximately, the proportion of phenols present in the oil, as described on page 399. On the other hand, the phenols are not the only constituents contributing to the odour of thyme oil, since linalol and borneol are present to the extent of about 5 and 8%, respectively. Thyme oils which have suffered abstraction of the greater part of their thymol frequently possess a very fair odour. The addition of *phenol* to thyme oil according to the United States Pharmacopœia, 8th Rev., may be detected by agitating the oil with a little *hot* water, when no blue or violet colour should be produced in the aqueous liquid on the addition of ferric chloride solution.

The less important varieties of thyme oil are described in the following table:

Oil	Botanical source. Root of:	Sp. gr.	Opt. rot.	Characters and constituents
Wild thyme..	*Thymus serpyllum*	0.890 to 0.920	$-10°$ to $-21°$	Cymene; a sequiterpene; one or more phenols.
....	*T. capitatus* *T. camphoratus*	About 0.900	....	Pinene; cymene; dipentene; thymol (?); carvacrol (?); bornyl acetate.

Turpentine Oil (Spirit of Turpentine).

Oil of turpentine is contained in the wood, bark, leaves, and other parts of pines, firs, and other coniferous trees, and is usually prepared by distilling, either with water or alone, the crude turpentine or oleoresinous juice which exudes from incisions in the bark of the trees. The non-volatile portion constitutes *rosin* or *colophony* (page 399), and the distillate, varying in yield from 10 to 25%, is the volatile oil or spirit

of turpentine commonly called "turps." *Rectified oil of turpentine* is obtained by treating the first product with alkali, to saturate any resin acids, and redistilling, preferably in a current of steam.

The principal forms of oil of turpentine are American and Russian. The so-called English or English-distilled turpentine oil is either American or Russian oil imported into or distilled in Great Britian, or a substitute derived from petroleum and mixed with more or less oil of turpentine. French turpentine oil is difficult to obtain and has ceased to be an article of ordinary commerce in Great Britain. Though presenting close resemblances, these forms are not strictly identical, as will be evident from the following description:

French turpentine oil is manufactured chiefly from the crude turpentine or "gum" yielded by the *Pinus maritima* (*P. pinaster*), but smaller quantities are obtained from the frankincense pine. Of late years the distillation has been conducted by blowing superheated steam into the still, no external heat being employed. To this improved method the constant character of the product is probably due. French oil of turpentine after neutralisation and rectification consists almost entirely of *lævopinene* or terebentene, which has already been fully described (page 179). Smaller proportions of other terpenes, of cymene, and of *resinous matters*, are also present in the commercial oil.

American turpentine oil is obtained from the turpentine collected in southern portions of the United States from several species of pine. Its main constituent is dextropinene or australene, having the same b. p., sp. gr., and chemical characters as the terebentene of the French oil, but differing from that body in being usually *dextro*rotatory. With this exception, and the fact that French oil of turpentine appears to absorb oxygen somewhat less rapidly than the American product, the characters of the two oils are practically identical.

According to J. H. Long, the greater part of American turpentine oil is obtained from the long-leaf pine (*Pinus Australis*). The "loblolly" or "oldfield" pine (*P. tæda*), the "pitch" pine (*P. rigida*), and the "swamp" or Cuban pine (*P. Cubensis*) supply comparatively small quantities only.

Russian oil of turpentine is chiefly the product of *Pinus sylvestris*, but *P. Ledebourii* and other species also contribute to it. A sample of Russian turpentine oil, of 0.8682 sp. gr., examined by W. A. Tilden, was found to contain from 10 to 15% of a pinene boiling at about the the same temperature as australene, but having the sp. rot. of 23.5°;

65 to 70% of sylvestrene; a considerable quantity of cymene; and
small proportions of viscid hydrocarbons boiling at high temperatures.
But Russian oil of turpentine is very variable in character, the normal
constituents being accompanied with more or less of the products of
the destructive distillation both of the rosin and the wood, including
benzenoid hydrocarbons, phenoloid bodies, furfurane or tetrol, and
sylvane.

The Russian turpentine oil of commerce is a very different product
from that obtained by distilling young leaves and cones of *Pinus syl-
vestris* with water (see Umney, *Pharm. J.* [4], 1895, 2, 542).

The sp. gr. of the Russian oil of commerce ranges from 0.8620 to
0.8722, and it contains matters not volatile at 100°, in proportions
ranging from 0.5 to 2.4 grm. per 100 c.c. (C. T. Kingzett, *J. Soc.
Chem. Ind.*, 1886, 5, 10). It has a characteristic odour, distinct from
that of American and French oils. It is not generally used in the
manufacture of paint, though there does not appear to be any good
reason against the use of the refined Russian oil for this purpose.
The oil finds a special application, under the name of "tar spirits,"
as a solvent of cotton-seed oil pitch for the manufacture of tar-varnishes.

The great readiness with which Russian turpentine oil absorbs
oxygen and becomes viscid specially adapts it for the manufacture of
the disinfectant known as *Sanitas*.

Swedish oil of turpentine is obtained from sources identical with
Russian product, which it closely resembles. A sample of so-called the
Swedish oil examined by L. Archbutt was a substitute, containing not
more than 10% of real oil of turpentine.

Finland Turpentine Oil.—The following results of the examination
of 3 samples of turpentine oil from Finland have been published
by Aschan and Hjelt (*Chem. Zeit.*, 1894, 18, 1566). The oil is
obtained from the trunks and roots of *Pinus sylvestris* and *P. abies*,
the distillation being conducted at a high temperature. The crude oil
is freed from acetic acid and tarry matters by distillation over lime.

Oil from South Finland.—Fractional distillation yielded 7.1%
boiling at from 155° to 160°; 30.2% boiling at from 160° to 165°;
22.6%, b. p. from 165° to 170°; and 20.1%, b. p. from 170° to 175.
The first fraction consists chiefly of pinene, the higher fractions
chiefly of sylvestrene and dipentene. This turpentine oil is therefore
identical in composition with Swedish and Russian oils.

Oil from North Finland.—The bulk of this oil distils at between

170° and 178°. The lower boiling portions consist chiefly of pinene, but the larger proportion of the oil consists of dipentene with scarcely any sylvestrene.

German turpentine oil, from *P. sylvestris, P. abies, P. vulgaris,* and *P. picea,* possesses a sp. gr. of 0.860 to 0.870 and a dextrorotatory power of from 15° to 20°. It contains pinene and sylvestrene.

Indian turpentine oil is obtained from *Pinus longifolia.* It has a sp. gr. of 0.8741 and an opt. rot. of 0° 43′.

Grecian turpentine oil is distilled from *Pinus halepensis.* Its sp. gr. is 0.8634, opt. rot. 77° 34′, and ref. index 1.4678.

Turpentine Obtained by Distilling Resinous Wood with Steam. —The chief fraction distils between 155° and 160°, and contains much pinene. In the higher fractions sylvestrene, but no dipentene, was observed. From this it is concluded that while sylvestrene occurs ready-formed in the resin of the northern coniferous trees, dipentene is not a natural product, but is formed by the superheating of the pinene during the process of distillation.

While exhibiting more or less characteristic differences in certain respects (*e. g.,* optical activity, b. p.), oils of turpentine from different sources present a close general similarity, and the following description, though applicable in particular to oils of American origin, may be accepted as generally accurate:

Commercial oil of turpentine has a peculiar characteristic odour and a pungent taste. The sp. gr. is said to range from 0.862 to 0.875, but, according to Parry, does exceed the limits 0.858 to 0.870, except Russian oil which reaches 0.875. French and American oils begin to boil between 156° and 160°, and fully 90% usually distils below 173°. Russian oil distils at a higher temperature, the greater part passing over between 165° and 190°. Old samples of turpentine oil leave a small proportion of non-volatile resinous matter on distillation. The optical activity differs with the source and is only of value as a guide to that point.

According to H. Schiff (*Chem. Zeit.,* 1896, **20,** 361), the odour commonly associated with oil of turpentine is due to the presence of a small proportion (under 1%) of an aldehydic oxidation product, which is formed when the oil is exposed to a feeble light in an imperfectly closed vessel. On treating the oil with sodium hydrogen sulphite solution this body is removed, and the purified oil retains only a slight ethereal aroma; but the characteristic odour soon returns if

the oil is exposed to the air. It is a noteworthy fact that the odours
of American, French, and Russian turpentine oils are quite distinct.

E. Kremers (*Pharm. Rev.*, 1897, **15,** 7) has recorded the following
figures yielded by a sample of crude oil of turpentine when subjected to
the purification by agitation with milk of lime and distillation in open
steam. 1 litre of the crude oil of sp. gr. 0.872 at 20° and rotatory
power $[a]_D = 11.616°$ was agitated with an equal volume of milk of
lime, and after an interval of at least 12 hours, distilled in a current
of steam, 4 fractions of 200 c.c. each being collected, and the residual
200 c.c. rejected:

Fraction	Sp. gr. at 20°	$[a]_D$
1	0.864	14.180
2	0.866	12.297
3	0.8702	11.420
4	0.8722	10.700

The decrease in volatility was, therefore, accompanied by a dimi-
nution of rotatory power, as has been noticed by others.   In another
similar experiment the whole (mixed) distillate was dried over anhy-
drous sodium sulphate. The oil possessed an agreeable odour, its
sp. gr. was 0.864 at 20° and sp. rot. 12.177°. Rectification over
milk of lime, in the manner described, results, therefore, in the pro-
duction of an oil of excellent quality.

Oil of turpentine is readily combustible, burns with a very smoky
flame, is almost wholly insoluble in water, glycerol, and dilute alka-
line and acid solutions. It is very soluble in absolute alcohol, but is
greatly reduced by the presence of water, spirit of 0.850 sp. gr. dis-
solving only 10% of its weight.

It is very soluble in (probably miscible in all proportions with) ether,
carbon disulphide, chloroform, benzene, petroleum spirit, and fixed
and essential oils.

Turpentine oil, even when clear, is never wholly free from water, and
on distillation the first fractions are usually turbid.   The *facile* forma-
tion of hydrogen peroxide in presence of turpentine oil and its subse-
quent decomposition into oxygen and water, may account for this fact.

Turpentine oil absorbs oxygen on exposure to air, gradually becom-
ing viscid and ultimately resinous. It is this property which gives
turpentine oil its peculiar value—not shared by its substitutes—to

the painter and varnish-maker, since it acts as an oxygen-carrier to the drying oil, and the resin formed acts as a binding material for the pigments with which it is mixed.

Turpentine oil in contact with water is gradually converted into *terpin hydrate*. When acted on by sulphuric acid terebene is produced (page 426).

Chlorine and bromine combine with oil of turpentine with such energy that inflammation frequently occurs with separation of carbon. When dissolved in carbon tetrachloride or chloroform, turpentine oil absorbs very nearly 2 molecules of bromine. Iodine is dissolved by turpentine oil to form a green solution, which ultimately becomes hot and gives off hydriodic acid; and when considerable quantities of iodine and turpentine oil are suddenly brought together, explosion frequently ensues. When distilled with bleaching powder and water, turpentine oil yields a considerable proportion of chloroform.

Moderately strong nitric acid oxidises turpentine oil to resinous bodies, which ultimately yield terebic acid, terpenylic acid, oxalic acid, acetic acid, and other products. Ordinary turpentine oil yields terephthalic and paratoluic acids in addition, but these products are chiefly due to the oxidation of the cymene present, and are formed in traces only by the oxidation of pure pinene. Fuming nitric acid acts very violently on oil of turpentine, often setting it on fire.

Strong chromic acid mixture oxidises turpentine oil chiefly to acetic acid, but a weaker reagent produces terpenylic acid. If cymene be present, terephthalic acid appears among the products of the oxidation.

Further information respecting the chemistry of oil of turpentine is given on page 407.

While presenting close resemblances in most respects, the oils of turpentine from different sources exhibit differences which are more or less characteristic, in their optical activities, as shown in the table on page 406.

The oil shipped from Charleston comprises turpentine of somewhat high dextrorotatory power, as well as oil of the Wilmington and Savannah types. Other American ports furnish a somewhat irregular product; but the values always lie between the extremes given in the table, and in the majority of cases the oils belong to the Wilmington type, Brunswick alone exhibiting a marked tendency to furnish a product of the Savannah type (H. E. Armstrong, *J.Soc.Chem. Ind.*, 1882, **1,** 478).

Source	Opt. rot.,°	Number of samples	Authority
French.			
Pure terebentene (*l*-pinene)......	− 40.4	....	W. A. Tilden.
Commercial oil	− 30 to − 30.5	....	H. E. Armstrong.
Commercial oil................	− 25.3	....	C. Symes.
American.			
Pure australene (*d*-pinene).......	+ 21.5	....	W. A. Tilden.
Oil shipped at Wilmington...... ..	+ 12.3 to + 16.3	35	H. E. Armstrong.
Oil shipped at Savannah........	+ 8.8 to + 12.0	12	H. E. Armstrong.
Oil shipped at Charleston	+ 9.5 to + 16.7	9	H. E. Armstrong.
Commercial samples	+ 12 to + 15.3	....	A. Wilson.
Oil from Columbia, S. C.........	− 2 to + 18.9	6	J. H. Long.
Oil from Wilmington, N. C.......	+ 8.3 to + 19.8	5	J. H. Long.
Oil from Mobile, Ala	− 34.8 to + 29.6	13	J. H. Long.
Commercial samples...........	+ 9.7 to + 16.9	13	J. H. Long.
Commercial samples.......... ..	+ 7.6 to + 15.9	11	L. Archbutt.
Russian.			
Pure sylvestrene	+ 19.6	....	W. A. Tilden.
Commercial oil........	+ 15 to + 23.4	23	H. E. Armstrong.
Commercial oil	+ 15 to + 22.2	67	C. T. Kingzett.

Adulterations of Turpentine Oil.—The most usual adulterants of oil of turpentine are certain fractions of petroleum known as "turpentine substitute," and "rosin spirit," which is the more volatile portion of the product obtained by distilling ordinary rosin. Certain fractions of shale oil and coal-tar are not improbable adulterants, but their employment is not common. The table on page 407 gives a number of distinctions between real turpentine oil and its substitutes.

The *index* of *refraction* of turpentine oil is a useful indication of its purity, especially in confirmation of other tests. Genuine oil of turpentine was found by T. Macfarlane (*Canadian Inland Rev. Dept.*, 1901, *Bull.* 79) to have a ref., index ranging from 1.4667 to 1.4722 at 20°. Rosin spirit ("spiritine") has a similar refractive index, while light petroleum products and kerosene have lower refractive indices than oil of turpentine (see table, page 407). Macfarlane's observations were made at the temperature of the laboratory, and were corrected to 20° by the addition or subtraction of o.0005 for each 1° above or below this temperature. The instrument was an Abbé-Zeiss refractometer, and was adjusted to read 1.3330 for water at 20°.

The *optical activity* often affords valuable information as to its origin and general character. The adulterants derived from shale and petroleum oils are always optically inactive, and those from rosin very frequently so, but turpentine oil always exhibits more or less rotation, unfortunately. The optical activity of genuine samples, even from the

CHARACTERS OF TURPENTINE OIL AND SUBSTITUTES.

	Turpentine oil	Rosin spirit	Petroleum naphtha	Shale naphtha	Coal-tar solvent naphtha
1. Index of ref..........	1.4667 to 1.4722	1.4701	1.4668	....	1.4341
2. Opt. activity........	Active.	Variable.	None.	None.	None.
3. Sp. gr.........	0.858 to 0.875	0.856 to 0.880	0.700 to 0.740	0.700 to 0.740	0.860 to 0.875
4. Temperature of distillation..	156 to 180	Gradual rise.	Gradual rise.	Gradual rise.	Gradual rise.
5. Action in the cold on coal-tar pitch.	Readily dissolves pitch to a deep brown solution.	Readily dissolves pitch to a deep brown solution.	Very slight action	Very slight action	Readily dissolves pitch to a deep brown solution.
6. Behaviour with absolute phenol at 20.	Homogeneous mixture.	Homogeneous mixture.	No apparent solution.	Homogeneous mixture crystallising on cooling.	Homogeneous mixture.
7. Behaviour on agitating 3 measures of the cold sample with 1 measure of castor oil.	Homogeneous mixture.	Homogeneous mixture.	Liquid separates into 2 layers of nearly equal volume.	Behaves like petroleum naphtha.	....
8. Bromine absorption, dry..........	203 to 236	184 to 203	10 to 20	60 to 80	....
9. Behaviour with sulphuric acid......	Almost completely polymerised.	Polymerised.	Very little action.	Considerable action.	Moderate action.

same locality (page 406), is so irregular as to give the figures for
the optical rotation but little quantitative value.

The *sp. gr.* of turpentine oil, given in the table on p. 407, includes the
widest range observed in genuine commercial samples. R. G. Dun-
wody found a number of samples of *commercial oil of turpentine* to
range in sp. gr. from o.856 to o.876 before rectification, and from
o.851 to o.873 after rectification. In the case of genuine samples,
an exceptionally high sp. gr. is due to the presence of oxidation
products. The sp. gr. increases rapidly on keeping unless precau-
tions are taken to exclude air and light. T. Macfarlane (*Canadian
Inland Rev. Dep.*, 1901, *Bull.* 79) found the average increase of a num-
ber of samples of oil of turpentine to amount to 3.4% of their weight.
The increase for different samples was very different. Rosin oil and
light petroleum products do not appreciably increase in sp. gr. on
keeping.

Somewhat sharper figures characterise the sp. gr. of turpentine oils
from different sources. Thus:

Range of sp. gr. at 15.5°	Kind of oil	Number of samples	Observer	Reference
o.8650 to o.8695	American	20	A. Wilson	*Chem. Trade J.*, 1888, **6**, 316.
o.8622 to o.8655	American, dis-tilled in laboratory	13	J. H. Long	*Chem. Trade J.*, 1892, **10**, 261.
o.8656 to o.8748	American (commercial samples)	....	J. H. Long	*Chem. Trade J.*, 1892, **10**, 261.
o.8615 to o.8706	American	157	L. Archbutt	Communicated.
o.8617 to o.8696	Russian	8	L. Archbutt	Communicated.

The sp. gr. is in itself sufficient to indicate the presence of any con-
siderable proportion of some adulterants of turpentine oil, but it is not
of much value for quantitative purposes, owing to the variable charac-
ter of the shale and petroleum products. In fact, heavier fractions of
shale oil and petroleum are apt to be added to turpentine oil, although
their presence is still more objectionable than the naphthas.

J. H. Long (*Chem. Trade. Jour.*, 1892, **10**, 261) has suggested the
determination of the vapour density of turpentine oil as a method for
its technical examination. A specimen of the pure oil was distilled,
and about o.150 grm. of the fraction passing over between 155.5°
and 156.5° examined by the V. and C. Meyer method (*Ber.*, 1878,
11, 2253), ethyl benzoate being used as the heating liquid. 2 experi-
ments showed a vapour density of 4.68 and 4.66, corresponding to

molecular weights of 135.1 and 134.5. Unfractionated commercial turpentine oil showed vapour densities ranging from 4.73 to 5.11. Samples of light petroleum products naturally gave lower figures.

The behaviour of turpentine oil with coal-tar pitch, phenol, and castor oil affords simple and useful tests for its purity; but the indications must be accepted with caution as the tests fail to detect certain adulterants even when present in considerable proportion. Thus R. G. Dunwody has pointed out (*Amer. J. Pharm.*, 1890, **62**, 284) that a sample consisting of 35% of turpentine oil with 65% of petroleum spirit will give a homogeneous mixture with castor oil. He states that both petroleum spirit and turpentine oil are perfectly miscible with pure *glacial acetic acid*, but that a fairly sharp distinction between them is obtainable by using glacial acetic acid containing 1% of water, since oil of turpentine is miscible with an equal measure of 99% glacial acetic acid, whereas petroleum is not. Dunwody gives the following figures which, however, require verification with other samples of petroleum and turpentine oil:

Petroleum	1	2	3	4	5	7	8 c.c.
Oil of turpentine	9	8	7	6	5	3	2 c.c.
Measure of acetic acid containing 1% of water required for solution.	40	60	80	110	150	230	270 c.c.

Squire and Caines (*Pharm. J.* [4], 1902, **14**, 512) found that some samples of turpentine oil gave clear solutions with 99% acetic acid, but that others gave turbid solutions. Pure glacial acetic acid always gave clear solutions. The British Pharmacopœia (1898) states that oil of turpentine is soluble in its own volume of glacial acetic acid. According to W. Duncan, however (*Chem. and Druggist*, 1901, **58**, 474), many genuine samples require up to 5 parts of acetic acid for complete solution, and the test cannot therefore be relied upon as conclusive evidence of adulteration. Rosin oil and rosin spirit are both readily miscible with glacial acetic acid.

B. Redwood has stated that the presence of petroleum spirit in turpentine oil is readily and certainly indicated by the reduced flash-point of the sample. Thus, while genuine American turpentine oil flashes at 33.3°, the addition of as little as 1% of ordinary petroleum spirit lowers the flash-point by about 12.2°. This statement has been traversed by Parry, who finds that the flash-point of genuine turpentine oil, as determined by Abel's close-test apparatus, ranges from 33.3° to 37°. Archbutt states that genuine oil of turpentine flashes at 32.2°.

J. H. Long, in a valuable paper (*Chem. Tr. J.*, 1892, **10**, 261), has given the flash-points and densities of mixtures of 95% of American turpentine oil, flashing at 32°, with 5% of such petroleum products as could be used for the sophistication of turpentine oil. The flash-point of a mixture is naturally reduced by the presence of the more volatile products, but is actually raised by the oils of higher density. The sp. gr. of any mixture can be calculated from those of its components. Long also gives the following figures for the sp. gr. and distillation temperatures of various petroleum products. By the term "initial temperature" of distillation Long means the point at which about 1 c.c. of the 100 c.c. employed will have passed over:

Product	Sp. gr.	Distillation temperature	
		Initial	Final
Gasolene............ 88° B...........	0.6508	About 40°	About 110°
Gasolene......... .... 74° B.........	0.7001	About 55°	About 125°
Benzine............... 63° B.........	0.7306	About 95°	About 165°
"Standard White".....110° fire test......	0.7999	About 130°	Above 360°
"Water White". . ....150° fire test......	0.7918	About 140°	About 310°
"Headlight........ ....175° fire test......	0.7952	About 160°	About 315°
Mineral seal oil.	0.8293	About 230°	Above 360°
Paraffin oil........................ ..	0.8906	About 300°	Above 360°
Oil of turpentine.	0.8680	About 156°	About 185°

It will be noted that the observed rotations of commercial oils of turpentine differ considerably from the sp. rot. powers of the terpenes said to form their chief constituents. J. H. Long has pointed out that the optical activity of commercial oil of turpentine of American origin is far more irregular than is commonly assumed. Thus, while the great majority of specimens of American oil exhibit a marked dextrorotation, samples are occasionally met with which are only feebly dextrorotatory or which even exhibit lævorotation. In 2 cases the dextrorotation reached 29.6 and 25.1° respectively, an activity which is greater than that attributed by Tilden to pure australene. Out of forty samples examined by Long (some of which were American oils of commerce and others prepared by him in the laboratory by distilling the fresh oleo-resins in copper with water) 3 samples exhibited lævorotation ($-2.02°$, $-34.83°$, and $-16.92°$). Long finds the oil from the *spruce-pine* (*Pinus glabra*) to be strongly lævorotatory, the angular rotation in a 200 mm. tube ranging from about

−63° to over −70°. On fractionally distilling the oil, the portions first passing over showed an angular rotation of −69° to 73° (for 200 mm.), which fell in the fractions of higher b. p: to about 10° less. Long has further shown that the rotation of the fractions of oil of turpentine frequently becomes less and less in the higher fractions. In one case the optical rotation fell to 2°, while another sample gave on distillation a first fraction which had a rotation of −16.8 and a twelfth fraction having a rotation of −4.4°.

Long suggests that the lævorotation sometimes exhibited by American turpentine oil may be due to products from spruce-pines, especially from trees in the district around Mobile. He points out that in numerous oils known to be free from spruce a marked dextrorotation was always observed, while low dextrorotation was limited to oils distilled in districts where the spruce-pine is occasionally found. Long affirms that turpentine from the same tree contains lævo- and dextro-pinene in varying proportions (*J. Amer. Chem. Soc.*, 1899, **21**, 637). The observation of Marsh and Gardner (*J. Chem. Soc.*, 1891, **59**, 725) that the first fractions obtained by the distillation of turpentine oil have a greater optical activity than those of higher b. p., is confirmed by Long. In one case, the last fraction was *lævorotatory*, a fact that Long suggests may have been due to the presence of the hitherto unknown *lævocymene*.

Exposure to light or to air has been observed to increase the optical activity of turpentine oil. By submitting American oil of turpentine to fractional distillation, Armstrong obtained a portion having a sp. rot. of +24.8°, and by submitting the original oil to air-oxidation and subsequently distilling off the unaltered hydrocarbon in a current of steam he several times obtained products of considerably higher rotatory power than the original oils. Similarly, the hydrocarbons carried over by the air current during the oxidation of Russian turpentine oil are almost free from sylvestrene and usually exhibit a higher rotatory power than the original crude turpentine from which they are derived.

Fractional distillation, if carefully conducted, probably affords more information as to the origin and purity of oil of turpentine than any other single test, and if the optical activity of the fractions be also observed further light will be thrown on the nature of the sample. Genuine American oil of turpentine commences to boil at 156°, or within a degree or so of that temperature, the greater part passing

over before the thermometer rises above 162°. As a rule, 90% or more
passes over before the thermometer rises above 173°, and the distil-
lation should be practically complete below 185°. Russian turpentine
oil distils chiefly between 165° and 190°. On the other hand, petro-
leum, shale, and resin products commence to distil at very varying
temperatures, according to their quality, but during the distillation
the thermometer rises regularly through a considerable range.

The exact behaviour of a sample of turpentine oil on distillation
depends materially on the precise manner in which the operation is
conducted, and in any series of experiments, the results of which are
meant to be comparable, the same conditions should be rigidly ob-
served. Of course, the most perfect separation of the constituents is
obtained by the use of a dephlegmator; but, for ordinary purposes,
the distillation of the turpentine oil in a retort heated over a naked
flame, with the thermometer bulb immersed in the liquid, will be found
very satisfactory. The distillation should be conducted exactly in the
manner described for the assay of commercial benzols.

The following table shows the behaviour of samples of genuine
American oil of turpentine when fractionally distilled in Allen's
laboratory, without dephlegmator, the thermometer bulb being
immersed in the liquid:

	1888	1888	1888	1899	1899
Sp. gr.	0.8696	0.8720	0.8754	0.8662	0.8666
Opt. rot.	....	....	....	12.75°	14.0°
Refractive-index	....	....	....	1.4687	1.4685
Fractional Distillation.					
Barom. pressure in mm	....	....	....	758	....
First drop collected at	157	157.5	157	155	155
5 % at	....	....	....	157	....
10 % at	158	158.5	159	157.5	....
20 % at	158.5	159	160	158	....
30 % at	159	159	161	158.5	....
40 % at	159	160	161	158.5	....
50 % at	159	161	162	158.5	156
60 % at	159	161	162.5	159	....
70 % at	160	161.5	164	160	....
80 % at	161	163	164.5	161	....
90 % at	163	167	176	163.5	....
93 % at	....	....	200	167	160
96.3 % at	....	200	....	172	....
97.3 % at	200	....	....	....	165
97.5 % at	....	....	....	174.5	....
Residue	1.61% thick; treacly	2.43% clear; treacly	4.44% deep brown; very viscous	0.40% yellow-ish	yellow-ish
Bromine temperature reaction	....	....	....	16.9°	16.5°
Iodine number	....	....	....	385.8	....
Oil surviving polymerisation, %	....	....	....	1.75	3.50

The following figures show the behaviour of 2 samples of *rosin spirit* of English manufacture, when 100 c.c. measure was distilled in Allen's laboratory in 1886, without dephlegmating arrangement, the thermometer being immersed in the liquid:

	Sample A (Liverpool)	Sample B (Hull)
Sp. gr. at 15.5°	0.8703	0.8955
Sp. rot. $[a]_D$	+0.87°	+12.75°
Fractional Distillation.		
First drop over at	149%	150%
Distillate below 155°	4.5	2.0
Distillate below 160°	9.5	4.5
Distillate below 170°	19.0	11.0
Distillate below 180°	33.5	18.5
Distillate below 190°	57.5	30.5
Distillate below 200°	69.5	41.5
Distillate below 210°	74.5	50.0
Distillate below 220°	77.5	57.5
Distillate below 230°	81.5	62.0
Distillate below 240°	84.0	65.5

These figures illustrate the irregularity of commercial rosin spirit. Sample B had an optical activity equal to most American oils of turpentine, but the results of the fractional distillation show that only a small proportion of true turpentine can have been present.

The following figures, communicated by L. Archbutt, also show the behaviour of samples of turpentine oil, believed to be genuine, when distilled under the conditions already described. A Fahrenheit thermometer was employed, and the centigrade temperatures shown in the table are calculated from the observed figures:

Measure of distillate from 100 c.c.	American oil			Russian oil		
	Range of temperature	Average temperature	Number of samples	Range of temperature	Average temperature	Number of samples
1 c.c.	156.0 to 163.9	160.1	94	161.1 to 164.5	163.1	4
5 c.c.	156.5 to 165.0	161.0	103	163.9 to 169.4	167.0	8
90 c.c.	162.0 to 176.4	169.7	103	177.2 to 188.9	181.6	8
95 c.c.	162.8 to 186.0	174.1	103	181.7 to 215.5	190.8	8
96.5 to 98 c.c.	163.9 to 205.5	180.4	103	187.8 to 208.9	199.5	7

The figures given in the table on page 415 were also obtained by Archbutt by the examination of various turpentine adulterants and substitutes.

According to J. McCandless (*J. Amer. Chem. Soc.*, 1904, **26,** 981), adulteration with refined wood spirits (wood turpentine) may be detected as follows, after kerosene has been shown to be absent by the polymerisation process (page 416): 100 c.c. of the oil is slowly distilled with a low flame, and the refraction figure of the first o. 5 c.c. measured at 25°. In the case of genuine turpentine oil this is never below 60°, usually 61° to 63°. Several samples of wood turpentine showed readings from 57° to 59°. Wood turpentines which do *not* show a low initial reading nearly always show a high reading on the final portion of the distillate. For the 97th and 98th c.c. of the distillate the reading in the case of a genuine sample never exceeds 77, according to McCandless, and is usually much less, while with wood turpentine the reading may reach 90. A further distinction noticeable during distillation is that while about 95% of oil of turpentine generally distils below 165°, this proportion of distillate is not reached in the case of wood turpentines until a much higher temperature is attained.

For the approximate estimation of petroleum naphtha in oil of turpentine and its isolation therefrom, H. E. Armstrong (*J. Soc. Chem. Ind.*, 1882, **1,** 480) recommended a process dependent on the ready and nearly complete polymerisation of oil of turpentine by sulphuric acid, and the comparative indifference to such treatment of the paraffins which form the greater part of petroleum spirit. The method as modified by Archbutt is as follows: 500 c.c. of the sample of turpentine oil are placed in a stoppered bottle and treated with 120 to 170 c.c. of a mixture of 2 measures of strong sulphuric acid with 1 measure of water (2 : 1). The mixture is cautiously agitated at first, the bottle being kept thoroughly cool by a current of cold water. The turpentine is gradually converted into a viscid oil, and when this has taken place, and no more heat is developed on repeated agitation, the liquid is transferred to a separator and the acid layer tapped off. The oily layer is then transferred to a flask and subjected to steam-distillation. When all that is volatile in a current of steam has passed over, the oily portion of the distillate is separated from the aqueous layer and treated with half its volume of sulphuric acid previously diluted with 1/4 of its volume of water (4 : 1). The mixture is agitated as before, the acid liquid separated, and the oily layer again distilled with steam.

CHARACTERS OF ADULTERANTS AND SUBSTITUTES OF TURPENTINE OIL.

	Rosin spirit			Camphor oil	Eucalyptus oil	So-called "Canadian turpentine"		"Terebo"	"Imported spirit"	"Blended turpentine"	"English distilled turpentine"
	A	B. Old sample	Rectified			A	B				
Sp. gr. at 15.5°	0.8569	0.8884	0.8838	0.9135	0.8902	0.8185	0.7844	0.8263	0.8057	0.7982	0.8188
Distillation temperature:											
1 c.c.	148.9	142.2	160.6	180.0	129	172.2	117	152.2	154.0	151.5	155.6
5 c.c.	155.6	150.0	167.8	188.3	162	173.9	119	156.7	156.0	153.5	156.7
90 c.c.	197.2	249.0	279.4	226.1	189	272.2	160	193.3	234.6	189.5	196.7
95 c.c.	210.0		310.0	234.4	201	300	162	315.6	235.6	202.0	205.0
Iodine number, %	272.6	178.5	166.9	130.2	110.0	172.8	162.8	58.2	2.6	31.8	107.4
Oil surviving polymerisation test (page 416): %	4.4					46	54.9				
Sp. gr.						0.766	0.725				
Flash-point (Abel test), °F		86					37	72	78	79	81

	"English turpentine"	"Siberian turpentine"	"South American turpentine"	Turpentine substitute	Turpentine substitute	"Beadless solvent"	"Beadless solvent"	Petroleum distillate	"Turpolene"	"Patent turpentine," 6 samples
Sp. gr. at 15.5°	0.8570	0.8603	0.8227	0.8162	0.8238	0.8072	0.8093	0.7992	0.8189	0.8005 to 0.8220
Distillation temperature:										
1 c.c.	151.0	162.8	157.8	164.4	162.8	156.7	162.8	157.8	160.0	154.4 to 163.3
5 c.c.	153.9	164.4	158.9	167.2	165.0	159.4	163.9	158.9	163.3	160.0 to 170.6
90 c.c.	181.1	170.7	193.9	222.8	218.9	226.7	225.6	192.8	222.2	232.0 to 250.0
95 c.c.	187.8	181.1	200.7	231.1	227.2	238.9	236.1	201.1	229.4	246.1 to 261.1
Iodine number, %	273.7	266.8	121.6	20.3	55.2	4.8	4.9	4.0	39.4	12.0 to 21.6
Oil surviving polymerisation tests (page 416): %		4								
Sp. gr.										
Flash-point (Abel test), °F	78	101	87	80	90	85	91	91	85	72 to 84

When genuine turpentine oil has been operated upon, the volatile product of this second treatment consists merely of cymene and a small quantity of a *paraffinoid hydrocarbon* ($C_{10}H_{20}$). It never exceeds 4 or 5% of the measure of the original sample, and with care is as low as 3%. If the volume notably exceeds 5% *it* is advisable, as a precaution, to repeat the treatment with 4 : 1 acid. In any case, the residual oil should then be violently agitated with 4 times its volume of undiluted sulphuric acid at 60°, this treatment being preferably repeated. The residual hydrocarbon is then separated, steam-distilled, and again measured, when the surviving oil from pure turpentine oil, either American or Russian, will not exceed 1 . 5% by measure of the original sample. Any excess over this proportion represents the *minimum* admixture of *petroleum naphtha* present.

H. Herzfeld employs a somewhat similar method, using strong and fuming sulphuric acid for the polymerisation of the turpentine oil when the mineral adulterants separate on standing.

Shale naphtha suffers considerably by the foregoing treatment with acid, and cannot be satisfactorily estimated by the process. Its proportion is best deduced from the results of a bromine titration; but the estimation is at best only approximate.

Evidence of the presence of *rosin spirit* is also afforded by the increased yield of hydrocarbons on treatment with 4 : 1 and concentrated sulphuric acid, as rosin spirit also yields a cymene and paraffinoid hydrocarbon on treatment with 4 : 1 acid, but no sharp estimation can be effected by the method, which would even allow a considerable proportion of the admixture to escape detection. The cymene from rosin spirit being isomeric with that from turpentine, proof of the presence of rosin spirit might possibly be obtained by examining the cymene produced.

The following modification of Armstrong's method has been suggested by J. M. McCandless (*J. Amer. Chem. Soc.*, 1904, **26**, 981; and private communication to Mr. Allen) as a means of detecting small quantities (1% and over) of petroleum products. The method depends upon the observation of the ref. index (in the Zeiss butyro-refractometer) of the unpolymerisable residue: 100 c.c. of the oil is placed in a 600 c.c. flask, and gradually mixed with 50 c.c. of concentrated sulphuric acid with constant cooling and agitation. 25 c.c. of water is then added and the contents of the flask distilled in a current of steam until a total distillate of 100 c.c. is obtained. The ref. index is now determined

on a few drops of the separated oil in the distillate. The remainder
is measured approximately, and violently agitated with an equal vol.
of fuming sulphuric acid in a dry stoppered flask. The resulting
mixture is poured into cold water, the oil separated, and steam-distilled
until 100 c.c. of distillate has been obtained. The ref. index of the dis-
tilled oil is again taken, after which the remainder is
treated with twice its vol. of fuming sulphuric acid,
and the foregoing operations repeated. Expressed
in terms of the centesimal scale of the refractometer
(at 25° with sodium light), the oil from the third
polymerisation never gives a lower reading than 30
in the case of pure turpentine oil or wood, while
with oils containing only 1% of kerosene the reading
is as low as 25, and can be slowly reduced to 22 by
continued treatment with fuming sulphuric acid.
The method is not strictly quantitative, but the final
vol. obtained may be regarded as the minimum
proportion of petroleum present, if the refractometer
reading does not exceed 22. Adulteration with
petroleum naphtha or kerosene of low flash-point
results in still lower readings.

J. Marcusson and G. Winterfeld (*Chem. Zeit.*,
1909, 987) describe the following method for esti-
mation of mineral oils in turpentine: A special
apparatus shown in Fig. 6 is used. 30 c.c. nitric
acid (sp. gr. 1.52) are placed in the bulb *a* and
cooled to —10°. 10 c.c. of the sample are placed
in the stoppered funnel and allowed to fall drop by
drop into the acid taking about 45 minutes to intro-
duce and frequently agitating. The mixture is then
kept still for 15 minutes at the above-noted temper-
ature; the stoppered funnel is removed and ordinary
nitric acid (cooled to —10°) added until the oily
portion of the liquid in the bulb is brought into the neck. Its vol. is
read off when it has acquired room temperature, the bulb being
meanwhile on the freezing mixture. The mineral oil may be removed
by a pipette and tested as usual.

FIG. 6.

W. M. Burton (*Amer. Chem. J.*, 1890, **12,** 102) recommends that,
instead of polymerising the oil by sulphuric acid, the sample should be
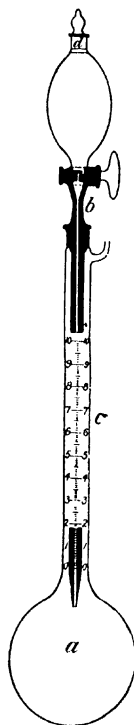
treated with cold concentrated nitric acid, whereby the turpentine is readily oxidised to various acids of the aliphatic and aromatic series soluble in hot water, while petroleum is but slightly affected. Burton recommends for the operation the use of a flask of 750 c.c. capacity, fitted with a doubly perforated cork. Through one hole is inserted the tube of a tapped funnel having a capacity of 100 c.c., while the other carries a tube connected with an inverted condenser. About 300 c.c. measure of nitric acid of 1.5 sp. gr. is placed in the flask, and 100 c.c. of the sample of oil of turpentine measured into the separating-funnel. The flask is immersed in cold water and the turpentine then allowed to fall drop by drop into the acid, with frequent agitation. Violent action takes place with evolution of red fumes. When the turpentine oil has all passed into the flask the apparatus is allowed to stand until all action is over. The contents are transferred to a large separating-funnel and treated with successive portions of *hot* water. In this way all the products resulting from the action of the acid on the terpenes are removed, while any petroleum paraffins remain insoluble in water and can be readily separated and measured. Benzene if originally present is converted into nitrobenzene in this process and can be steam-distilled from the aqueous liquid, and then rectified by redistillation.

J. H. Long states that Burton's method has given him fairly good results. Allen considered the method, even when very carefully conducted, too dangerous for general use, actual explosions having occurred, especially when pure or nearly pure turpentine is under treatment. With largely adulterated samples, the petroleum acts as a diluent, and the action is comparatively moderate. As a supplementary treatment, after applying the Armstrong process, Allen found the Burton method to be occasionally useful. It should never be applied direct.

A good indication of the presence and amount of some adulterants is obtainable by distilling the sample in a current of open steam. Unless it has been freely exposed to the air for some time, genuine turpentine oil leaves a mere trace of non-volatile matter, but old samples may leave a small proportion (up to about 3%) of resinous matter, which solidifies on cooling. According to Armstrong, if more than 0.4% non-volatile residue is left after steam distillation, it consists, as a rule, of *petroleum oil*. This is recognisable by its comparatively low sp. gr. (0.800 to 0.850, colophene being 0.940) and more or less marked blue fluorescence when dissolved in ether. The residue from

genuine old turpentine oil is readily oxidised and dissolved by dilute nitric acid, while the petroleum product is more or less nitrated without altering much in volume. *Rosin oil* would be recognisable by the Storch-Morawski reaction (see Vol. II, p. 310).

The analysis of turpentine oils by fractional distillation with steam has been the subject of a special investigation by W. C. Geer under
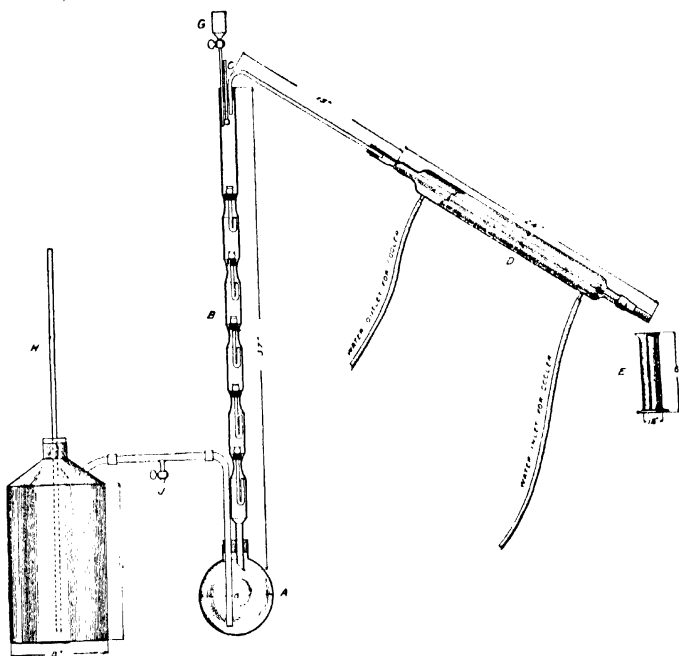

FIG. 7.—From circular 152, Forest Service U. S. Department of Agriculture.
By W. C. Geer.

the auspices of the U. S. Forestry Service. The results have been made public in Circular 152 of that bureau. The annexed illustration (Fig. 7) shows the special form of distilling apparatus, the supporting clamps being omitted. F is the source of steam, H a safety tube, G a dropping-funnel, alongside of which is a thermometer, C. Graduated cylinders (E), about 100 c.c. capacity, receive the distillates, about fifteen of these will be required. Corks may be used for connec-

tions. The special construction of the still-head is an important feature. The foundation is an ordinary soft-glass tube about 4 cm. in diameter provided at regular intervals with constrictions, the widest being at the top. Traps are made by inserting small glass U-tubes of different lengths, supported by brass wire-gauze collars. The thistle-expansion at the top prevents the tube's falling. Each trap is about 6 mm. shorter than the one above. A strip of 40-mesh brass wire gauze about 1 cm. wide is wrapped about each tube as a collar until this is large enough to fit its particular constriction snugly. The U-tubes are then dropped into the column. It is a matter of some skill to set up the dephlegmator, but after being once adjusted it is ready for a long series of determinations. It can be cleaned after turpentine distillation by the ordinary solvents, alcohol and ether, without taking it apart. Before using, it is necessary that each of the bent tubes be filled with water, which is accomplished by pouring water slowly into the tube held upright.

To perform an analysis, the boiler F is about half-filled and the funnel G entirely filled with water. The flask A is dried and weighed (to within 0.010 grm.), 500 grm. of the sample weighed into it, and connected with the condensing apparatus as shown. A sample of the original oil should be preserved for comparison with the several fractions of the distillate. The steam is then started, and when it escapes freely through the valve J, this should be closed and the burner turned down so as to give a rate of oil-distillation of about two drops per second. The burner under A should be regulated so as to prevent excessive condensation, and both burners should be surrounded by asbestos shields. The water is also allowed to drip slowly from G at the rate of about one drop per second so as to keep liquid on the brass collars.

At the beginning of the distillation it is necessary to watch the still carefully and occasionally relieve the steam pressure through J until the dephlegmator is evenly heated and the rate of reflow uniform in each section.

In the operation the receiver is changed according to the nature of the distillation. If the temperature remains fairly constant the receiver need be changed only rarely, but if rapid temperature changes occur more fractions should be taken. The temperature is, of course, recorded each time the cylinder is changed. Generally about a dozen fractions are collected. The cylinder is previously weighed dry and

then after having received the fraction. The difference is the com-
bined weight of water and oil. It is sufficiently accurate to take the
volume of the water in c.c. as equivalent to its weight in grm. and the
weight of distilled oil can be thus ascertained.

Geer found by using a very pure wood turpentine that in ascertaining
sp. gr. of the fractions, a correction of 0.00083 should be added for
every degree C. above 15° at which observation is made and the same
amount subtracted for every degree C. below.

For valuable analytic data and graphic representations of the
fractionation, the original bulletin should be consulted.

The oil which distils over in a current of steam will consist of the
genuine oil of turpentine, together with the more volatile portions of
any adulterants, and the presence of any shale or petroleum naphtha
will be indicated by the low sp. gr. of the oily portion of the distillate,
after separation from the water which condenses with it.

The use of *rosin spirit* as an adulterant of turpentine oil is frequent,
and if used in small proportion is difficult of detection. The odour
suffices to indicate the presence of an inferior spirit, but is useless
if the refined article has been employed. The behaviour on distilla-
tion varies, but the temperature rises regularly throughout the process,
and no considerable fraction is obtained at a constant temperature of
158° to 160°, as in the case of American turpentine oil. Very often
there is a notable residue of viscid oil left on steam distillation. The
bromine absorption of rosin spirit is somewhat lower than that of
turpentine oil, but the difference is not sufficiently marked or
constant to serve as a distinction. The opt. rot. of commercial
oil of turpentine is too variable to allow of the optical activity
being employed for the determination of the proportion of rosin
spirit present. The reduced flash-point is a trustworthy test for the
presence of rosin spirit.

According to H. E. Armstrong, the products of the distillation of
rosin are always optically inactive; but this is certainly not uniformly
the case with the oridnary commercial products. The sp. rot. of rosin
spirit in Allen's experience ranges from 0° to 13°. The heavier frac-
tions obtained by the distillation of rosin, commonly known as "rosin
oil," are viscous liquids of high b. p., and quite unsuited for the ad-
ulteration of turpentine oil. Hence the recommendation of A. Aignan
(*Compt. rend.*, 1897, **124,** 1367) for the estimation of "rosin oil" in
oil of turpentine has little practical interest. Similarly, the index of

ref., the observation of which is recommended by M. Zune (*C. r.*, 1893, **114**, 490) for the estimation of "rosin oil," has little value in practice.

F. Evers (*Chem. Centr.*, 1898, **1**, 865) states that the Custom House official method for the examination of turpentine oil depending upon the increase of temperature with an equal vol. of hydrochloric acid (sp. gr., 1.19), is useless owing to the facts that the older and more resinified the oil, the greater the rise of temperature with hydrochloric acid; and that mixtures of such oils with "patent" oil of turpentine gave results similar to those of genuine samples. Evers employs a method for the detection of such substitutes for oil of turpentine, depending on the fact that the substitutes do not combine with bromine, while oil of turpentine takes up an appreciable quantity. His method has been improved by Schreiber and Zetzsche (*Chem. Zeit.*, 1899, **23**, 686), who recommend the following procedure: The sample is first dissolved in sufficient alcohol of about 95% strength to yield a 2% solution. 2 other solutions are required—1 containing 50 grm. of potassium bromide and 15 grm. of potassium bromate in 1000 c.c. of water; and a dilute sulphuric acid solution, 1 : 3. 20 c.c. of the turpentine solution in alcohol are treated with 20 c.c. of each of these solutions, and the mixture shaken for 1/2 minute, the temperature being kept near 20°. Genuine oil of turpentine decolourises this solution.

A. McGill (*Canadian Inland Rev. Bull.* 79, 34) finds the improved method fairly satisfactory. Coal oil, gasoline, and rosin oil failed to decolourise the bromine solution; 20% of coal oil could easily be detected in admixture with genuine turpentine oil, but 10% gave only a doubtful indication.

A test for rosin spirit in turpentine oil has been described by P. H. Conradson (*J. Soc. Chem. Ind.*, 1897, **16**, 519). An aqueous solution of sulphurous acid, when shaken with rosin spirit, colours the latter yellow, the aqueous layer remaining colourless. Pure oil of turpentine, benzene, gasolene, and "160° oil," give no such colouration. After standing for several hours, the yellow obtained with rosin spirit changes on the surface to brown and further to blue, finally becoming a reddish or bluish-brown. Oil of turpentine shows no change of colour on standing with sulphurous acid solution. A snow-white emulsion is produced on shaking the mixture, and the emulsion breaks up very slowly. A sample of "wood turpentine" examined by Conrad-

son gave the above coloration with sulphurous acid, had a sp. gr. of 0.845, a flash-point below 80° F., and was evidently adulterated.

The *iodine absorption* of turpentine oil is capable of furnishing valuable information, and may aid in distinguishing between American and Russian oil of turpentine. L. Archbutt, as the result of a large experience, recommends the employment of the Wijs method. Hübl solution, unless recently prepared and of full strength, does not give the maximum absorption. The time allowed for the reaction between the Wijs solution and the oil of turpentine must be exactly the same for all samples, as this factor has a great influence upon the amount of iodine absorbed. Although absorption of iodine is very rapid at first, the maximum absorption ($C_{10}H_{16} + 2I_2 = 374\%$ iodine) is not reached for many hours. This is shown by the following results communicated to the author by Archbutt. In each experiment 0.1 grm. of oil of turpentine was used, and 30 c.c. of the Wijs' solution, containing 0.7674 grm. of iodine.

Time of action	Wijs' value of American oil of turpentine		
	A	B	C
5 minutes	277.4		
10 minutes	290.3		
20 minutes	316.1	324.2	318.7
1 hour	338.1		
6 hours	359.8		
18 hours	379.4	379.3	373.4
24 hours	382.6		

Archbutt recommends 20 minutes' action as the most convenient, and states that samples of American oil of turpentine which absorb less than 320% of iodine from Wijs' solution in this time should be regarded with suspicion. For the estimation, a few mg. more than 0.5 grm. of the sample is weighed into a 50 c.c. flask, which is then filled to the mark with chloroform. The solution having been well mixed, 10 c.c. is transferred to a stoppered bottle and mixed with 30 c.c. of Wijs' solution containing not less than 0.7 grm. of iodine. After exactly 20 minutes' action an excess of potassium iodide solution is added and the liquid is titrated in the usual manner. At the end of the experiment, the unabsorbed iodine should be at least equal in

amount to that absorbed, and not more than 5% in excess of the amount absorbed (Archbutt). If these conditions do not obtain, the test is repeated with suitably altered proportions of iodine and turpentine oil.

The iodine values of various substitutes and adulterants of oil of turpentine are given on page 415. These were determined by the Hübl method.

The *bromine thermal test* (O. Hehner, *J. Soc. Chem. Ind.*, 1897, **16**, 87) also affords a rapid method of obtaining an approximation to the iodine value, but presents no advantage over Wijs' modification of the latter.

The price of American turpentine oil has risen considerably of late years, and refined Russian turpentine oil is now being employed for many purposes. In addition, during the last 3 or 4 years a product termed "wood turpentine" ("pine turpentine" or "stump spirits") has been manufactured by distilling pine-wood scraps with superheated steam at 260°. 2 qualities of oil are obtained, and both grades of mechanically refined oil are stated by the manufacturers to be equal to true oil of turpentine in most respects, though this is doubtful. Considerable quantities of this product are being sold as pure turpentine oil.

The following results have also been communicated by Archbutt:

| | Iodine absorption (Wijs) | | | | | | |
| | American turpentine oil | | | | Russian turpentine oil | | |
Time of action	Number of samples	Highest	Lowest	Average	Number of samples	Highest	Lowest
20 mins.......	30	348.1	309.3	329.0	2	295.5	276.5
18 hours......	18	395.2	364.0	377.2	2	354.7	333.5

Wood Turpentine.

Wood turpentine oil is stated to have a similar sp. gr., b. p., and distillation characters as pure oil of turpentine. J. M. McCandless has pointed out certain small differences in these properties (see page 414). There is, however, a marked difference in odour between the 2 products. Wood turpentine oil is said to contain both terpenes and alcoholic constituents. According to R. A. Worstall (*J. Soc. Chem.*

Ind., 1904, **23**, 302), wood turpentine may be readily detected by its low iodine number, as determined by the Hübl solution after 12 hours' action in the dark with a large excess of iodine. Under these conditions, Worstall found the average absorption of pure turpentine oil to be 375% of iodine, while wood turpentine gave the value 212, and a sample of turpentine oil containing even 5% of wood turpentine yielded the low figure of 360% of iodine absorbed. The figure 370 is suggested by Worstall as the minimum limit of iodine absorption for genuine turpentine oils under the above conditions. The results of J. M. McCandless (*loc. cit.*) show that the iodine absorption of wood turpentine may thus vary from 282 to 352%.

The following description of the characters of genuine oil of turpentine is substantially that of T. Macfarlane (*Canad. Inland Rev. Dept., Bull.* 79), and is based upon the results of a large number of analyses: Oil of turpentine is a clear and practically colourless liquid, but is made decidedly opaque by shaking with 0.1% of water, and perfectly clear samples give, when distilled, a first fraction of 10%, which is opaque but which settles clear in a few hours. The odour of turpentine oil is peculiar and characteristic, quite distinct from that of gasoline, rosin spirit or acetone, and capable of disguising these odours to the extent of 10% admixture. The sp. gr. of turpentine oil lies between 0.860 and 0.880 (usually about 0.870) at a temperature of 15.5°, but samples which have been long exposed to air may have a higher sp. gr. When distilled, the first fraction amounting to 1/10 of the original volume has a sp. gr. between 0.856 and 0.870. The sp. gr. of the residual tenth (undistilled) should not exceed 0.900. The b. p. should lie between 154° and 158°, and 90% should distil below 180°. On evaporating the sample at 100°, the fixed residue should not exceed 2%. The flash-point by Abel's test should be about 32°. Turpentine oil should dissolve completely in an equal volume of glacial acetic acid, and the first 10% fraction obtained by distillation should similarly dissolve. 1 c.c. of a solution of 1 part of asphaltum in 10 of turpentine oil should not, after filtration, be rendered translucent when diluted with 9 c.c. of turpentine oil. The ref. index at 20° should lie between 1.4667 and 1.4722; while that of the first fraction (of 10%) should not exceed 1.4700. Concentrated sulphuric acid should polymerise and char the oil at 100°. Turpentine oil should respond to the bromine test of Schreiber and Zetzsche (described on page 422).

The German law requires that oil of turpentine employed for the denaturation of alcohol shall have the following characters: Sp. gr., between 0.855 and 0.865 at 15°. When 100 c.c. measure is fractionally distilled in a metal flask furnished with a dephlegmator, not more than 5 c.c. must come over below 150°, but at least 90 c.c. at 160°. When 20 c.c. of the sample are shaken vigorously with an equal volume of water. and the liquid allowed to stand till clear, the upper (turpentine) stratum must measure at least 19 c.c.

A. and P. Andouard (*J. Pharm. Chim.* [6], 1902, **15,** 99) have described a petroleum product from America, known as "white spirit," which is much used in France for the adulteration of oil of turpentine. "White spirit" has a violet-blue fluorescence, and a sp. gr. of 0.807. It is almost optically inactive, and begins to distil between 150° and 160°, the last fractions having a high b. p. It leaves about 40% of residue at 205°.

An article sold in commerce as "*German oil of turpentine*" is stated to consist of a mixture of camphor oil with petroleum fractions.

Banner's "*turpentine substitute*," according to the specification (Brit. Patent, 1885, 12249), is essentially prepared by selecting, during the distillation of petroleum, coal oil, or other similar heavy hydrocarbons, groups of fractions containing hydrocarbons of a sp. gr. ranging from 0.730 to 0.840. The characters of 6 samples examined by Archbutt are given in the table on page 415, under the heading "Patent Turpentine."

Terebene, according to the British and United States Pharmacopœias, is a mixture of dipentene, and other hydrocarbons, obtained by agitating oil of turpentine with successive quantities of sulphuric acid until it no longer possesses optical activity. The product is then distilled with steam. Some manufacturers of terebene do not carry the process sufficiently far to produce a totally optically inactive product.

Terebene is a colourless liquid with an agreeable thyme-like odour and an aromatic terebinthinate taste. It is only slightly soluble in water, but dissolves in 3 vols. of 90% alcohol. On exposure to air and light, terebene gradually resinifies, becoming yellowish and acid. The sp. gr. of terebene ranges from 0.862 to 0.866 at 15.5°. Terebene should be optically inactive. The British Pharmacopœia requires that terebene should not contain more than 15% of constituents distilling below 165°, and that all except a slight viscid residue should distil between 156° and 180 (absence of excess of resin).

According to the United States Pharmacopœia (8th Rev.), terebene distils between 155° and 165°. Terebene should not redden moist blue litmus-paper, and should yield only a very slight non-volatile resinous residue on evaporating 10 c.c. in an open dish at 100°.

Tyrer and Wertheimer (*Pharm. J.* [4], 1900, **11**, 101) find that, with due precautions, American oil of turpentine yields terebene answering the official requirements, except in the respects that 5% remains undistilled at 180°, and that no fraction is absolutely devoid of optical activity. 2 samples of "terebene" examined by these observers boiled considerably above the official limits, and had thus been distilled by steam under pressure or by a direct flame. Terebene from French oil of turpentine was found on fractional distillation to yield 28% of a mixture of optically-inactive substances.

Painters' terebine, which is a dark brown solution of manganese and lead soaps in oil of turpentine, used as a drier by painters, must not be confounded with *terebene*.

Wormseed Oil (Levant Wormseed Oil).

This oil should not be confused with the oil of "American wormseed," which is in reality chenopodium oil. Levant wormseed oil is usually from the unexpanded flower-buds of *Artemisia maritima*, but, according to Parry, other species probably contribute.

The true wormseed oil is a thick yellow or brownish oil, having the camphoraceous odour of cineol. It has a sp. gr. of 0.930 to 0.935. These figures represent the usual limits of sp. gr. The outside limits, as given by Gildemeister and Hoffmann (*The Volatile Oils*), are 0.915 to 0.940. The oil is slightly lævorotatory. When rectified, it is colourless.

The constituents, so far as known, are cineol, together with another oxygenated body which has not yet been identified, and, possibly, dipentene.

Chenopodium Oil (American Wormseed Oil).

This is derived from the fruit of *Chenopodium ambrosioides* (*C. anthelminticum L*). It is a light yellow oil. According to Schimmel & Co., samples from absolutely reliable sources had a sp. gr. of about 0.970 and were soluble in 10 volumes of 70% alcohol. The oil shows an optical rotation ranging from —5° to —18°. It probably contains

limonene. The United States Pharmacopœia (8th Rev.) requires the official oil to be soluble in 5 vols. of 70% alcohol and to have an opt. rot. of not less than —5°.

Gane and Webster (*Amer. Drug. and Pharm. Rec.*, **54**, 163) give reports of examinations of the ordinary adulterants of turpentine oil, see also *Pharm. J.* [4], 1909, **23**, 684.

Wormwood Oil (Oil of Absinthe).

This oil is obtained by the distillation of the green herb *Artemisia absinthium*, which is extensively cultivated in North America. It is often called absinthe oil.

Wormwood oil is dark green or greenish-blue, and has a strong odour and acrid taste. Its sp. gr. ranges from 0.925 to 0.955. Adulteration with oil of turpentine may, therefore, be inferred from lowered sp. gr. Since wormwood oil contains only slight traces of pinene, the presence of turpentine in the oil may also be detected by the characters of the first 10% of the distillate. The distillate from pure oil dissolves in 2 vols. of 80% alcohol to a clear solution. Very small additions of turpentine oil, which is a frequent adulterant of oil, may thus be detected. The opt. rot. of the oil cannot well be taken owing to its deep colour, but since the chief constituent, thujone, is strongly dextrorotatory, the oil will no doubt be optically active in this direction.

The principal constituent is a ketone thujone (see page 212). Thujyl alcohol is also present to a considerable extent, as well as thujyl esters of acetic, isovaleric, and palmitic acids. Phellandrene is present to a very small extent, and pinene only in slight traces. A sample of the pure oil examined by Schimmel & Co. was found (upon acetylation and saponification) to yield 24.2% of thujyl alcohol, of which 13.9% was present in the form of esters (equivalent to 17.6% of thujyl acetate).

Japanese wormwood oil (Yomugi oil), from *Artemisia vulgaris*, is bright green and has a marked odour of cineol, which it contains, and probably also thujone. Schimmel & Co. found it to have the following characters: Sp. gr., 0.9101; opt. rot., —13.25°; acid value, 1.56; ester value, 29.81. The oil was not completely soluble in alcohol.

Terpeneless Essential Oils.

By subjecting the essential oils to careful distillation under reduced pressure, there are obtained as distinct fractions, the hydrocarbons or terpenes of the oils, and an odorous oxygenated portion, which can be kept behind in the distillation apparatus. The terpene fraction has comparatively little or no odour in most cases; while, as a rule, the oxygenated or high-boiling fraction retains all the good qualities of the original oil in a heightened degree. In other words, the oil has been concentrated, and the residual valuable fraction is found to have a far greater solubility coefficient (in alcohol) than the original oil, a fact which is of considerable commercial importance. In certain cases, distillation at however low a pressure would cause decomposition of the valuable oxygenated constituents of the oil. When this is the case, the terpeneless oil is of very little value since it does not represent the unaltered concentrated oil. Some few oils contain so little terpene that the terpeneless oil possesses little advantage over the natural product.

The chief constituents of essential oils, prepared in a pure state (e. g., citral, eugenol, safrole, etc.) have occasionally been termed terpeneless oils, but this is manifestly a misnomer. In many cases these products are inferior to the real terpeneless oils, though sometimes they are superior to the latter. The 2 classes should, however, be carefully differentiated and the term "terpeneless oil" restricted to the product properly coming under that description.

Völckel and Schweitzer in 1840 and Haensel in 1876 first pointed out the value of this procedure. Many other observers followed up their researches and the increased usefulness of the terpeneless products has been widely recognised. The terpenes as a class readily oxidise and resinify on exposure to air, and at the same time develop an unpleasant odour and taste. Essential oils, which are thus liable to lose their delicate odour and flavour on keeping, may therefore frequently be stored in a terpeneless state for a long time without deterioration. Thus the terpeneless oils are specially valuable in the manufacture of perfumes, liquors and essences, and for medicinal purposes.

The following table shows the physical characters of many of the best-known terpeneless oils. The data are chiefly due to Parry, though some are taken from H. Haensel's *Reports* (H.). With the exception of the first sample of bergamot oil (see foot-note, page 430), all the samples were genuine terpeneless products.

Terpeneless oil	Sp. gr. at 15.5°	Opt. rot.,°	Vols. of alcohol required for complete solution
Angelica root.........	0.951 0.956 (H.)	—3.7°	....
Angelica seed.........	0.961 (H.)	—1.5°	1.8 of 80% 41 of 70% (H.)
Bay..................	1.034; 1.028 (H.)	....	5 of 60% (H.)
Bergamot[1](1).........	0.903	—11.25	....
Bergamot (2).........	0.8875	—9.25	8 of 60% (H.).
Bergamot (3).........	0.885	—7.9	....
Caraway[2].............	0.962 to 0.965	+55 to +59	(B. p., 223°–225°) ....
Citronella............	0.932; 0.912	—5	....
Cloves...............	1.072	0	....
Eucalyptus...........	0.938 (H.)	—1.7	($[n]_D$, 1.4679)
Fennel...............	0.982	+12 to +24	....
Geranium............	0.896	—1.9	....
Ginger...............	0.909; 0.919 (H.)	....	1 of 80%; 45 of 70% (H.).
Juniper[3].............	0.916	—28.75	....
Lavender.............	0.893 to 0.897	—3 to —5	20 of 60% (H.). Contains 18–25% l i n a l o l; 30–40% linalyl acetate.
Lemon[4]..............	0.896 to 0.900	—7 to —9	5–20 of 70%; 260 of 60%; contains 42– 67% of aldehydes.
Lemon-grass.........	0.897	—1.2	....
Limes (expressed).....	0.896	—8.6	....
Limes (distilled)......	0.920	—2.2	....
Orange..............	0.894	+5 to +10	2 of 70% (H.).
Peppermint (various)..	....	—13 to —28 (H.)	....
Pimento.............	1.062	—0.5	....
Rosemary............	0.939; 0.944 (H.)	+10.9 (H.)	....
Sassafras	1.088	+2	....
Spearmint............	0.945 (H.).	....	70 of 70% (H.).
Wormwood...........	0.922	....	2.5 of 70% (H.). ·

[1] Probably contained artificial linalyl acetate (Parry).
[2] Reasoning from the figures yielded by this oil, Parry concludes that the physical characters usually ascribed to carvone are incorrect; probably the sp. gr. of carvone is about 0.964 and its optical rotation not more than 60°.
[3] Although free from terpene, this oil of course contains much sesquiterpene.
[4] Burgess and Child have recorded a number of figures showing the composition and behavior on fractionation of terpeneless oils of lemon (*J. Soc. Chem. Ind.,* 1901, **20**, 1176).

The "concentrated oil of lemon" on the market contains about 10% of terpenes and is therefore to be distinguished from the terpeneless oil. True terpeneless oil of lemon is freed from the greater portion of the natural stearoptone by allowing the latter to separate after the distillation of the terpenes; or the oil is prepared by distilling 90% of natural oil of lemons under reduced pressure, and steam-distilling the residue, when the terpeneless oil comes over practically free from citraptene. The yield of terpeneless oil is from 5 to 6%, containing approximately half its weight of *citral.* (See page 352.)

TABLE

OF CHARACTERS AND CONSTITUENTS OF ALL THE BETTER-KNOWN ESSENTIAL OILS.

The following tabular list of the characters of the better-known essential oils has been compiled from data given in E. J. Parry's *Chemistry of Essential Oils*, 2d Ed.; Bush & Co.'s *Reports (B. & Co.)*; Schimmel & Co.'s *Semi-Annual Reports (S. & Co.)*; and from current literature.

The table was originally prepared (for the 3d edition of this work), at the request of Mr. Allen, by A. R. Tankard and John Evans, and has been revised by Leffmann and LaWall.

TABLE OF ESSENTIAL OILS.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot.°	Other characters	Known constituents
Acacia	Flowers of *Acacia cavenia*.				Eugenol (40 to 50%); methyl-eugenol; methyl-salicylate (8%); benzyl alcohol (20%); benzaldehyde; geraniol; anisic aldehyde and probably also linalol, decyl aldehyde, and ionone.
	Flowers of *Acacia farnesiana*.				Similar to above, but eugenol is absent.
Achillea (see also *Ina Oil*).	Flowering herb of *achillea coronopifolia*.	0.924		A deep blue oil, with an odour of tansy.	Esters of tiglic and angelic acids, isobutyl isobutyrate, antheniol esters.
	Herb of *A. nobilis*...	0.905–0.915		Camphoraceous odour and bitter taste. Ref. index 1.4455.	Terpenes; a sesquiterpene; linalol; linalyl acetate.
		0.935	−10.4	Distils at 170°–265°.	
Ajowan	Fruit of *Carum ajowan*. (Carum). *Psychosis* S. & Co.	0.900–0.930	+1.0 to +1.5		Thymol, 40–50%; cymol.
	Herb of *carum ajowan*	0.900–0.930 0.860	+0.7	A light brown oil, sol. in 6 parts 90% alcohol, with separation of a paraffin.	Thymol (about 1%); phellandrene (trace).
Allspice	(*See Pimento Oil.*)				
Almond oil (bitter)	Fruit of *amygdalus communis*, var. *amara*.	1.045–0.171	Inactive.	Ref. index 1.542 to 1.551	Benzaldeyde, C_6H_5COH, over 90%. Hydrocyanic acid 2 to 4%.
Ambrette	S. & Co. B. & Co.	0.900–0.905 0.9145		Congeals at 10°. Deposits a paraffinoid hydrocarbon.	
Ammoniacum	The gum-resin from the stem of *Dorema ammoniacum*.	0.890	Slightly +	Distils between 250° and 290°	

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot.,°	Other characters	Known constituents
Angelica	Root of Archangelica (Angelica) officinalis. B. & Co.	0.855-0.905 / 0.8925	+26.7 to +30.1 / 15.0	Turns yellow on exposure to light. Saponification number. 37.7. Distils chiefly between 66°-70°.	Phellandrene; valeric acid; hydroxy-pentadecoic acid.
Japanese.	Fruit of A. officinalis. Root of Angelica refracta and Angelica anomala.	0.850-0.900 / 0.915	+11 to +12	Pale yellow; darkens in colour with age. At 16°, crystals of a fatty acid separate melting at 62-63°. Oil distils between 170°-300°.	Phellandrene; valeric acid; hydroxy-myristic acid.
Angostura	Bark of Galipea cusparia.	0.930-0.960	-36 to -50		Cadinene; galipol, $C_{15}H_{26}O$, 14%; galipene; an oxygenated body; pinene.
Anise	Fruit of Pimpinella anisum.	0.980-0.990	To -1.9	At 15°-19° solidifies to a white, crystalline mass (anethol). B. pt., 234°. Ref. index, 1.552 to 1.558.	Methyl-chavicol; about 90% anethole; anise-ketone.
Anise	Bark from Madagascar. Botanical origin uncertain.	0.969	-0.8		Methyl-chavicol; small amount of anethole.
Anise, Star (Chinese) [Badiana oil].	Fruit of Illicium verum.	0.980-0.990	0 to -12	At 12°-18° solidifies. Ref. index, 1.552 to 1.558.	Anethole; anise aldehyde and ketone; anisic acid; methyl-chavicol; estragol; pinene; phellandrene; safrole; ethyl-ether of quinol.
Anise, Star (Japanese) [Badiana oil].	Leaf of Illicium religiosum.	1.006	-8.1		Anethole; safrole; eugenol; a terpene (limonene?).
Apopin (Shu-yu)	From one of the Lauraceæ.	0.9279	+17.3		Camphor; eugenol; safrole; cineol; dipentene.

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot.°	Other characters	Known constituents
Arnica	Rhizome of *Arnica montana.*	0.990–1.000	−2.0	Yellow colour, becoming darker with age.	Dimethyl ether of thymo-quinol (80%); phlorol iso-butyrate, (20%); a very little phloral methyl-ether.
Artemisia	Herb of *Artemisia glacialis* (so-called *Genepi des Alpes*). Herb of *Artemisia vulgaris* (common mugwort).	0.969 / 0.907; 0.920		Distils at 195°–310°. Solidifies at 0° to a buttery mass.	Cineol; a fatty acid, m. p. 61°. Pinene (?); a substance containing $C_{10}H_{14}O$; the sulphuretted bodies, $C_{11}H_{18}S_2$; $C_{10}H_{16}S$; $C_{10}H_{18}S_2$; a blue fraction.
Asafoetida	The gum-resin from root of *Ferula foetida*, etc.	0.975–0.990	−9.25		Dextro- and lævopinene, 2%; alcohols, including geraniol, 35%; methyl-eugenol, 37%; and a deep blue fraction.
Asarum Canadense	Rhizome and root of *Asarum Canadense* ("Canada snake-root").	0.930–0.960	−3.5	Yellowish-brown oil.	Pinene; methyl-eugenol; asarone, but no asarol; a blue fraction.
Asarum Europaeum	Rhizome and root of *Asarum Europæum* ("Asara-bacca").	1.015–1.070		Thick, brownish liquid…	
Backhousia citriodora	Leaves of *B. citriodora.*	0.895	Inactive or slightly —.	R. index. 1.4890. Distils 215°–230°.	Aldehydes, 95% (chiefly citral); sesquiterpenes (traces); an amyl-ester (?).
Badiana	(See *Anise Oils*)				
Balsam-fir	Leaves of *Abies balsamea.*	0.894	−29		Bornyl acetate; pinene (?).
Basil (Basilicum)	Fresh herb of *Ocymum basilicum.*	0.909–0.990	−22 to +16		Pinene; cineol; camphor; linalol; methyl-chavicol.

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot.°	Other constituents	Known constituents
Bay (Myrcia)...........	Leaves of *Pimenta acris.* S & Co.	0.975–0.990 0.965–0.995	.... Up to −2.	Clove-like odour and spicy taste. Ref. index 1.487 to 1.585.	Eugenol and chavicol (60–65%); methyl-chavicol; methyl-eugenol; citral; myrcene; *l*-phellandrene.
Californian.	Leaves of *Laurus Californica.*	0.930 to 0.950	....	Ref. index 1.4785.	Cineol; terpineol (?).
Bergamot.....	Fresh fruit of *Citrus bergamia* (by expression).	0.88?–0.886	8 to 20	Greenish or greenish-yellow liquid. Begins to distil at about 170°. Ref. index 1.465 to 1.470.	Limonene; dipentene; linalol; linalyl acetate (36–39%).
Betle.........	Leaves of *Piper betle.* Dried leaves from Siam. Fresh leaves from Manila. Fresh leaves from Java.	.... 1.034 1.044 0.958	.... +2.8		Betle-phenol (para-eugenol); cadinene; sometimes chavicol.
Boldo........	Leaves of *Peumus boldus.* Dried leaves	0.8?6 0.915 to 0.945	−6.5	Distils 175°–250°.	Eugenol (?); pinene; cuminal; acetic esters; an oxygenated body; a sesquiterpene.
Boronia......	*Boronia polygalifolia.*	0.839	+10	Sweet odour resembling tarragon and rue. Distils largely between 150° and 190°.	
Buchu........	Leaves of *Barosma serratifolia.* Leaves of *B. betulina.*	0.944 0.969 0.9573	.... —48	Strong, mint-like odour. Ref. index 1.4800. The sp. gr. given refers to that of the oil after the diosphenol had separated at ordinary temperature.	Diosphenol (small amount); limonene; dipentene; menthone. Diosphenol (large amount); otherwise like above oil.

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot.,°	Other characters	Known constituents
Cajuput............	Leaves of *Melaleuca leucadendron.*	0.917-0.930	To −3	When crude, is a bluish-green liquid with a camphoraceous odour and somewhat bitter taste. Green colour usually due to traces of copper. Ref. index 1.460 to 1.466.	Cineol, about 50%; terpineol; terpenyl acetate; pinene (?); valeraldehyde (?); benzaldehyde (?).
Calamus...........	*Brit. Pharm.* Fresh herb of *Acorus calamus* (Sweet Flag). Rhizone. German {Fresh drug. Dry drug.} Japanese.	*Brit. Pharm.* 0.922-0.932 0.964 0.960-0.970 0.960-0.980 0.985-1.00	+20.7 +20 to +31 +15 to +21	Closely resembles the oil from the rhizome. Thick brownish liquid with a bitter taste. Ref. index 1.507 to 1.515. Much more soluble in dilute alcohol than the German variety.	Pinene (?); acetic, oenanthilic, haptylic, and palmitic acids; eugenol; asaryl aldehyde; asarone; calameone; parasarone; and a bluish fraction.
Camphor..........	By-product in preparation of common camphor by the distillation of wood of *Cinnamomum Camphora.* Leaves of camphor tree.	0.870-1.040 0.932	+12 to +32 +4.9	Very variable in character. Fractional distillation affords commercial light camphor oil (sp. gr. 0.920) and heavy oil (0.970). Liquid portions (separated from camphor) have properties of above camphor oils.	Pinene; phellandrene; dipentene; cineol; camphor; terpineol; safrol; eugenol; cadinene; camphene (?). Large amount of Camphor.
Camphor-wood (Venezuelan).	From Venezuelan wood of unknown origin.	1.155	+2.7	Solidifies to a crystalline mass (apiol) at ordinary temperatures.	Apiol (parsley-apiol), 90%.
Cananga..........	(See *Ylang-Ylang Oil.*)				

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot., °	Other characters	Known constituents
Canella.........	Bark of Canella alba.	0.922	....	Spicy odour and taste....	Pinene; caryophyllene; cineol; eugenol.
Caparrapi.........	Wood of Nectandra caparrapi.	0.915–0.935	—3	Pale yellow to brownish-red oil. Acid reaction to litmus. Odour sweet and resembling chloral.	Caparrapic acid (monobasic), melting at 84.5°; a sesquitepene alcohol (caparrapiol).
Caraway.........	Fruit of Carum Carvi. S. & Co.	0.905–0.915	75 to 85	Characteristic adour and spicy taste. Distils mainly above 200°. not more than 15% should distil below 185°. Ref. index 1.487 to 1.497.	Dextro-limonene; carvone; possibly carvacrol.
	Brit. Pharm.	0.910–0.920	....		
Cardamoms.........	Seed of Elettaria cardamomum. (Ceylon.)S. & Co.	0.936–0.946	+34 to +47	1.460–1.470	Terpinene; dipentene; limonene; terpineol; acetic esters.
	B. & Co.	0.895–0.905	+12 to +13	Camphoraceous odour and taste. Ref. index 1.4639	
	(Bengal.) S. & Co.	0.930–0.940 0.920	+30 —12.7	Distils chiefly below 220°. Ref. index 1.465.	Large amount of cineol.
Carrot (wild).........	Fruit of Daucus carota.	0.870–0.930	—13 to —37	Sharp taste............	Pinene; terpineol (?).
Cascarilla.........	Bark of Croton Eluteria.	0.890–0.930	+5	Ref. index 1.4800.........	Terpenes; palmitic and stearic acids (traces); cascarillic acid (2%); traces of eugenol and cresol; and oxygenated bodies.
Cassia.........	Bark of Cinnamomum cassia.	1.050–1.065	+1 to —1	Ref. index 1.585 to 1.605.	Cinnamic aldehyde, 70–85%; cinnamic esters.
Cedar-leaf (American).	Leaves of red cedar, Juniperus Virginiana. Commercial sample.	0.883–0.888	+55 to +65	....	Limonene; pinene (?); cadinene; borneol; bornyl esters.
		About 0.884	—8.25	Savin-like odour. Colourless.	
	S. & Co.	0.886	+59.1	Pale greenish-yellow. Medicinal properties probably similiar to the official oil of savin.	

TABLE OF ESSENTIAL OILS.—Continued.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot.,°	Other characters	Known constituents
Cedar-wood (American)	Wood of J. Virginiana.	0.940—0.960	−25 to −40	Ref. index 1.498 to 1.503.	Cedrene cedar-camphor.
Cedrat	(See Citron Oil.)				
Cedrela wood	Wood of Cedrela odorata.	0.9348	−0.3	Light blue..........	Probably cadinene.
Celery	Fruit of Apium graveolens.				Dextro-limonene, but no pinene (distinction from oil of turpentine); a very small quantity of palmitic acid and phenols; sedanolide, sedanonic acid.
	S. & Co. B. & Co. Green herb of A. graveolens.	0.880—0.890 0.8730; 0.8777 0.848—0.850	+67 +75; +71.6 +48 to +52		
Chamomile, German	Flower-heads of Matricaria Chamomilla.	0.930—0.945	Very slight.	Bluish colour, changing to green and brown on exposure to light. Bitter taste.	Solidifies to a buttery mass at a low temperature, owing to the presence of a paraffin, melting at 53°-54°. The oil appears to contain esters.
Roman.	Flower-head of Anthemis nobilis.	0.905—0.915	Slight.	Bluish colour when fresh, changing in the light to greenish or brownish-yellow. Burning taste. Ref. index 1.4455.	Isobutyl isobutyrate and angelate; amyl and hexyl tiglates and angelates; anthemol. The ester content appears to be much less than that of English oils (containing 80% esters).
	Brit. Pharm.	0.905—0.915			
Champaca. (See Guaiacum-wood Oil.)	Flowers of Michelia Champaca. Java. Manila.	0.914 0.938	−13.25 −54.1	Odour somewhat resembling oil of orris. Fragrant light brown liquid. Deposits abundant crystals at ordinary temperatures.	Benzoic acid or a benzoate.
	Flowers of Michelia longifolia. Java.	0.883	−12.8	Very volatile, odour resembling basilicum.	

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot., °	Other characters	Known constituents
Cheken-leaf..........	Leaves of Myrtus cheken.	0.880	+20	Yellow-green colour. pleasant odour.	Pinene; cineol.
Chenopodium (American wormseed).	Fruit of Chenopodium ambrosioides. Commercial Oils.	About 0.970	-5 to -6.3	Penetrating odour, and bitterish taste. Varies in character according to age.	
	Leaves of S. & Co. C. ambrosioides.	0.910 0.879	-19 -33	Odour of trimethylamine.	
Chervil..........	Seeds of Chærophyllum sativum.	....	....	Odour of anise and estragon oils.	Estragol; a paraffin.
Chione Glabra..........	Bark of Chione glabra (West Indies).	....	....	Curious and objectionable odour.	Ortho-hydroxy-acetophenone.
Cinnamon, Ceylon......	Bark of Cinnamomum zeylanicum.	1.025 to 1.035	0 to -1	Sol. in alcohol. Ref. index 1.590 to 1.599.	Cinnamicaldehyde; phellandrene; eugenol.
Cinnamon, Japanese....	(See Nikkei Oil.)				
Cinnamon leaf..........	From C. zeylanicum..	1.045 to 1.065	-1 to +1	Ref. index 1.5350........	Eugenol; cinnamic aldehyde; safrol.
Citron..........	Fresh peel of Citrus medica.	0.870	+66	....	Limonene; citral.
Citron (cedrat), expressed oil.	Fresh peel of Citrus medica (Citrea Gibocarpa).	0.851	+80	Ref. index, 1.475 at 20°. Contains minute white crystals.	Citral, about 6%; limonene; dipentene (?); a crystalline substance containing $C_{16}H_{18}O_4$.
Citronella..........	Grass of Cymbopogon (Andropogon) nardus	0.885-0.920	To -16	Ref. index 1.480 to 1.483 Java and Singapore oil 1.465 to 1.468.	Citronellal; geraniol; borneol; linalol; camphene; dipentene; limonene; methyl heptenone.
Citronella (Java Verbena).	Fruit of Tetranthera citrata.	0.895-0.980	....	Verbena-like odour, and has therefore been called "Oil of Verbena, Java."	Citral; a terpene.

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot., °	Other characters	Known constituents
Clove..........	Flower-buds of Eugenia caryophyllata. Brit. Pharm. S. & Co.	Not below 1.050. 1.045–1.070	Slightly lævo-rotatory (0° to 1° 30').	Boils between 250–260°, greater part distilling between 250–251°. Becomes darker and thicker with age. Spicy taste. Ref. index 1.530 to 1.535. Odour not so fine as true oil of clove.	Methyl alcohol; furfurol; 80–90% of eugenol; caryophyllene; acetyl eugenol.
	Flower stems........	1.040–1.065	To –1.3	Exceedingly agreeable cinnamon-like odour.	Methyl alcohol; furfurol; eugenol; caryophyllene.
Clove root	Root of Geum urbanum.				
Cochlearia (synthetic).		0.944 (at 12°)	....	B. p. 159–160°. In commerce a mixture consisting of oil of mustard and oil of rue is frequently sold as oil of cochlearia, but has not the properties of true oil.	Secondary butyl thiocarbimide.
Cognac..........	....	0.876–0.883	–0.05 to +0.75	Acid number 37 to 70; ester number 140 to 219; sol. in 2 parts of 80% alcohol.	
Conium..........	Fruit of Conium maculatum. Herb of C. maculatum.	0.831 0.931 at 20°	–2.2		
Copaiba..........	Oleo-resin of Copaifera Landsorfii, and other species. S. & Co.	0.890–0.910 0.900–0.910	Lævorotatory to –5 to –35 –8.1	Bitterish and pungent taste. Has same effects upon the system as copaiba.	Chiefly sesquiterpenes.
Coriander..........	Fruit of Coriandrum sativum. Brit. Pharm.	0.870–0.885	+7 to +14	Warm, spicy taste. Ref. index 1.4665.	Dextro-linalol (coriandrol); pinene.

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot., °	Other characters	Known constituents
Costus	Root of Aplotaxis lappa.	0.980–0.987	+15 to +16		•
Cubebs	Unripe fruit of Piper Cubeba. S. & Co. B. & Co.	About 0.920 0.910–0.930 about 0.930	... −30 to −40 −30 to −25	Pale greenish or yellowish oil, with a warm camphoraceous, aromatic taste. Ref. index 1.490 to 1.496	Chiefly cadinene, with some dipentene. When old, or distilled from old fruit, also contains cubeb camphor.
Cuilaban	Fruit of Cinnamomum Cuilavan.	1.051	...	Odour of eugenol; dark in colour.	Eugenol; methyl-eugenol.
Cumin	Fruit of Cuminum cyminum.	0.890–0.930	+4 to +6	Limpid liquid with a sharp spicy taste.	Cymol; cumin aldehyde.
Cypress	Leaves of Cypressus sempervirens. S. & Co.	0.882–0.887 0.892	+4 to +6 +16.5	Sol. 1: 2.5 of 90% alcohol.	d-Pinene; l-cadinene; furfural; d-camphene; d-sylvestrene; cymene; a ketone; sabinol; acetate of d-terpineol (m. p. 35°); valeric acid; cypress camphor.
Damiana	Turnera microphylla and other species.	0.940–0.990	−23.9	Greenish viscid liquid, with an odour of chamomile. Boils between 250° and 310°.	A blue oil in the higher fractions; a paraffin.
Dill	Fruit of Peucedanum graveolens. Brit. Pharm. East Indian. Anethum sowa.	0.895–0.915 0.905–0.920 0.970	+70 to +80 +7° +41.5	Penetrating odour, and afterward sweetish, sharp and burning taste. Odour quite different from East Indian dill oil. Ref. idex 1.480 to 1.495.	Limonene; carvone; a paraffin. Limonene; dill-apiol; carvone.
Dog-fennel	Entire plant of Eupatorium fœniculaceum.	0.935	+17.9		Phellandrene.

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot.,°	Other characters	Known constituents
Elder otto	Elder blossom (*Sambucus nigra*). B. & Co.	0.8461 (at 30°) 0.8277 (at 30°)	....	M. p., 28.2°; saponification number 75.4; after acetylation, 97.9. M. p., 28°.	Phellandrene; dipentene; the higher fractions probably containing polyterpenes and oxygenated compounds.
Elemi	Oleo-resin of Manila Elemi of uncertain botanical origin.	0.870–0.910	+45	Agreeable aromatic odour and taste.	
Elecampane	Root of *Inula helenium*.	....	....	....	Alantic acid; alanto-lactone; alantol.
Erigeron (or fleabane)	Fresh flowering herb of *Erigeron Canadensis*.	0.855–0.890 (increasing with age).	+52	Peculiar persistent odour and slightly pungent taste. Larger part distils between 175° and 180°.	Limonene; terpineol, and esters.
Eriodictyon	Leaves of *E. Californica*.	0.937	−1.6	Sol. in 70% alcohol.	
Estrogon (Tarragon)	Herb of *Artemisia Dracunculus*. S. & Co. Commercial oils.	0.890–0.960 0.920–0.960	+2 to +9 +2.5 to +9	Peculiar odour.	Methyl-chavicol.
Eucalyptus	(See page 336.)		+12 to +24		
Fennel	Fruit of *Fœniculum capillaceum* and other species. S. & Co. B. & Co. Commercial oils.	0.965–0.975 0.908 0.960–0.980	+7 to +22 +27.6 +6 to +20	Between 5° and 10° usually solidifies to a crystalline mass. B. p., 160° to 220°. Ref. index 1.525 to 1.534.	Pinene; phellandrene; dipentene; limonene; cymene (?); fenchone; anethol (usually about 60%). Oils from different sources never contain all these constituents simultaneously. Tardy found (in addition to some of the above) methyl-chavicol; anisaldehyde; anisic acetone; anisic acid; and unknown substance, containing $C_{11}H_{14}O_2$.

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot.°	Other characters	Known constituents
Feverfew	(See *Pyrethrum Oil.*)	0.900 to 0.960	....	....	Borneol and esters.
Fir-cone	....	0.860-0.875	-20 to -80	....	Pinene, limonene, bornyl acetate.
Fleabane	(See *Oil of Erigeron.*)	0.850-0.890	+50	....	•
Fœnugreek	Seeds of *Trigonella fænumgræcum.*	0.870	+8	Light brown oil; sol. in 90% alcohol.	
Frankincense	(See *Oil of Olibanum.*)				
Galangal	Rhizome of *Alpinia officinarum.*	0.915-0.925	-1 to -4	Boils between 170° and 275°; sol. in ½ part of 90% alcohol. Ref. index 1.480.	Cineol; eugenol (25%).
Galbanum	Gum-resin of *Ferula galbaniflua.*	0.910-0.940	-10 to +20	Yellowish oil of aromatic odour.	*d*-pinene; cadinene.
Gardenia	Fresh flowers.	1.009	+3.0	Boils at 204° with partial decomposition.	Benzyl acetate; styrolyl acetate; linalol; linalyl acetate; terpineol; methyl anthranilate; esters of benzoic acid.
Garlic	*Allium sativum.*	1.052	Inactive.	....	Allyl-propyl-disulphide; diallyl-disulphide.
Geranium (rose geranium).	Herb of several species of *Pelargonium*, especially *P. Radula, P. capitatum* and *P. odoratissimum.* Algerian. French. Réunion. Spanish. *S. & Co.* *B. & Co.*	0.890-0.898 0.894-0.899 0.886-0.895 About 0.898 0.906 0.885-0.905	-7 to -9 -9 to -12 -8 to -11 About -8 -16 -8 to -12	Pale yellowish or greenish (reunion) oil, having an agreeable rose-like odour. Ref. index 1.460 to 1.471.	Geraniol and citronellol (free, and combined as tiglates). Total alcohols 60 to 75% (of which 15 to 25% exist as esters).

TABLE OF ESSENTIAL OILS.—CONTINUED.

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Oil	Chief sources	Sp. gr. at 15°	Opt. rot.,°	Other characters	Known constituents
Geranium, East Indian (so-called Turkish geranium or Palmarosa oil).	From grass of a species of Andropogon, probably A. Schœnanthus. S. & Co. / B. & Co.	.... / 0.888–0.896 / 0.885–0.895	.... / −1.7 to +1.8 Not more than +1 or −1	....	Geraniol; geranyl acetate and capronate; dipentene; methyl heptenone (?). Total alcohols 75 to 95% (of which less than 10% exist as esters) consisting chiefly of geraniol, with very little or no citronellol.
Ginger...........	Rhizome of Zingiber officinale. B. & Co. { African. { Cochin.	0.875–0.885 / 0.8870 0.8820 / 0.8869–0.8998	−26 to −44 / −37.5 −45.3 / −12.4 to −27.4	Aromatic, somewhat burning taste. Ref. index 1.488 to 1.495.	Campene; phellandrene; l-zingiberene.
Ginger-grass oil........	....	0.930 to 0.945	+18 to +27	Ref. index 1.4850.	Geraniol.
Golden rod (Canadian)	Flowering herb of Solidago Canadensis, etc.	0.859	−11.2	....	Contains 85% of terpenes, mainly pinene with a little phellandrene and dipentene; possibly limonene; borneol; bornyl acetate; cadinene.
Grains of Paradise......	Seeds of Amomum melegueta.	0.894	−4	Distils mainly at 257°–258°.	Body of formula, $C_{12}H_{20}O$.
Grape-fruit (shaddock)	Fruit of Citrus decumana.	0.865; 0.860	+94.5	Odour of bitter orange oil.	
Guaiacum wood ("balsam wood").	Wood of guaiacum species, probably Bulnesia sarmienti.	0.968 at 30°	−6.5 at 30°	Very viscid oil. Violet and tea-like odour, and crystalline at ordinary temperatures.	Crystallisable guaiac-alcohol, or m. p. 0° ("Champacol"). A sample of so-called "Champaca-wood oil" was found by S. & Co. to be Guaiacum-wood oil.
Gurjun balsam........	Balsam of Dipterocarpus species.	0.920–0.930	−35 to −106	Distils mainly at 255°–256°.	A sesquiterpene; small amounts of alcohols.

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at. 15°	Opt. rot.°	Other characters	Known constituents
Hedeoma, American...	Dried leaves and tops of *Hedeoma pulegioides.* U. S. Pharm. S. & Co.	.... 0.920–0.935 (at 25°) 0.925–0.940	.... +18 to +22 +18 to +22	Limpid liquid with a mint-like odour and taste. Forms a clear solution with 2 volumes or more of alcohol (70%).	Hedeomol pulegone. •
Hedeoma (Penny-royal).	Leaves of *Mentha pulegium.*	0.930–0.960	+17 to +23	Ref. index 1.4805........	Pulegone.
Hedychium..........	Flowers of *Hedy-chium coronarium.*	0.869	-0.5		
Helichrysum........	Flowering herb of *Helichrysum stoechas.*	0.873	....	Distils mainly between 155°–170°.	Pinene.
Hemp..............	Dried herb of *Cannabis sativa.*	0.932	-10 to -12	....	Terpenes; sesquiterpenes.
Indian.	Herb of *C. Indica* ...	0.930	....		Cannibene.
Heracleum..........	Fruit of *Heracleum Spondylium.*	0.86–0.88	+0.25	Acid reaction. B. p. 80°–300°.	Ethyl butyrate; hexyl and octyl acetates; octyl capronate.
Hop...............	Flowers of *Humulus lupulus.*	0.840–0.882	To +1	Ref. index 1.4775........	Humulene; geraniol; tetrahydro-cymene (?); terpenes.
Horsemint (see Monarad Oil).	Herb of *Monarda punctata.*	0.930–0.940	Slightly +	Yellowish-red or brownish-red colour and a strong thyme-like odour.	Thymol; cymol.
Hyssop.............	Herb of *Hyssopus Officinalis.*	0.925–0.940	-19 to -23	B. p. 170°–218°. Odour of thujone.	Possibly thujone or thujyl alcohol
Iva...............	Dried flowering herb of *Achillea moschata.*	0.932 to 0.934	....	Light blue colour. B. p. 170° and 260°.	Cineol; "ivaol," a mixture of oxygenated bodies of unknown constitution.
Jasmine...........	Flowers of *Jasminum grandiflorum.*	1.009–1.018	+2.5 to +3.5	....	Benzyl acetate; linalyl acetate; benzyl alcohol; linalol; indole; methyl anthranilate; jasmone.

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at. 15°	Opt. rot.°	Other characters	Known constituents
Juniper..........	Fruit of *Juniperus communis*. *Brit. Pharm.* S. & Co.	0.850–0.890 0.865–0.890 0.865–0.885	.... inactive or to −18	Becomes dark and thicker by exposure to air. Has a somewhat terbinthinate and bitter taste. Ref. index 1.474 to 1.488.	Chiefly pinene with some cadinene; juniper-camphor.
Kæmpferia..........	Rhizome of *Kæmpferia rotunda*.	0.890 to 0.900	+12	Odour at first of camphor, then reminding of estragon oil.	Cineol. Odour suggests probable presence of methyl-chavicol.
Kiku..........	Leaves of *Pyrethrum Indicum*.	0.880–0.890			
Kobushi..........	Fresh leaves and twigs of *Magnolia Kobus*.	0.9642	−1.1	Sassafras-like odour......	Safrol: probably also citral.
Kuro-moji (Japan)....	Wood of *Lindera sericea*.	0.890–0.915	−0.1	Balsamic odour........	Dextro-limonene; dipentene; terpineol; levocarvone.
Lantana..........	Herb of *Lantana camara*.	0.952	−0.25		Pinene; cineol; geraniol; eugenol; fatty acids.
Laurel..........	Leaves of *Laurus nobilis*.	0.920–0.930	−15 to −18		Umbellulone; cineol; eugenol; methyl-eugenol; l-pinene; safrol; fatty acids (traces).
California.	Leaves of *Umbellularia Californica*.	0.948	−22	Agreeable but afterward irritating odour. Sol. in 1.5 parts 70% alcohol.	
Lavender..........	Fresh flowers of *Lavandula officinalis*. *U.S. Pharm.* French flowers. S. & Co.	0.885–0.897	−3 to −9	Ref. index 1.462 to 1.4675	Linalol; linalyl acetate (30 to 45%); geraniol (?); sesquiterpene (?); small amounts of pinene and cineol.
	English Flowers. {S. & Co. {B. & Co.}	0.885–0.900 0.8838	−7 to −10 −9.8	The content of esters in the French oil is usually about 3 times as high as English oil.	Much cineol; limonene; linalyl acetate (7 to 10%); a sesquiterpene. Chiefly linalyl acetate (10.7% esters).

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot.,°	Other characters	Known constituents
Lavender	Spanish flowers	0.916; 0.912	+16.4; +13.3	....	These oils contained 3.15% and 3.4% of esters (as linalyl acetate), and 44.5 and 59.5% free alcohol (as linalol). They probably contained some lavender spike oil.
	Portuguese. Flowers of *L. pedunculata.*	0.939	−44.9	Indistinct and not very pleasant odour. Distils almost completely between 170–200°. Has an odour resembling rosemary and camphor.	Linalyl acetate 39%; thujone; cineol.
	Flowers of *L. dentata.*	0.926		Distils between 180–245°. Has an odour resembling rosemary and camphor.	Cineol.
	Flowers of *Lavandula Stæchas.*	0.942			
Lavender, spike	Flowering herb of *Lavandula spica.*	0.905–0.920	−3 to +7	Much less fragrant than the official oil. Has odour reminding both of rosemary and lavender. Ref. index 1.4660.	Pinene; camphene; cineol; linalol; camphor; borneol; terpineol (?); geraniol; practically no esters.
Ledum	(See *Marsh-tea Oil.*)				
Lemon	Fresh lemon-peel of *Citrus medica,* var. *limonum.*	0.857–0.862	+59 to +67	Bitterish taste. Ref. index 1.475 to 1.4775.	Limonene; citral; citronellal; and according to Umney and Swinton, geranyl acetate; possibly also other esters of geraniol and citronellol.
	Brit. Pharm.	0.857–0.860	+59 (not less).		
Lemon-grass (verbena). Indian Melissa).	Grass of *Cymbopogon* (*Andropogon*) *citratus.*	0.895–0.905	+1 to −3	Fragrant odour, reminding of lemon and verbena. Ref. index 1.483 to 1.488.	Citral; geraniol; methylheptenone.
	B. & Co.	0.9023	−12.7		Aldehydes, 28%; alcohols, 30%.
Lemon thyme	....	0.898	−3	Distils chiefly between 210°–230°.	Citral; thymol.

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot.°	Other characters	Known constituents
Lime, Italian	Rind of fresh fruit of *Citrus limetta* (by expression). Distilled oils.	0.882 0.870–0.875 0.8629–0.8656	+35 to +40 +58.25 +34.8 to +45	Golden-yellow oil, with refreshing odour. Ref. index 1.4770.	Limonene; citral; linalol; linalyl acetate (26%). Citral (6.3 to 8%); and "limene." $C_{10}H_{16}$.
Lime-flowers	Flowers of *Citrus limetta*.	0.870	+21.5		Linalol; methyl anthranilate.
Lime, West Indian (Limette).	Rind of fresh fruit of *Citrus medica*, var. *acida* (by expression). Distilled oil.	0.901 0.873–0.885 0.856–0.868	+36.3 +35 to +40 +46.6	Lemon odour. 18% of non-volatile residue. Ref. index 1.477 to 1.480. Unpleasant odour. 3% non-vol. residue.	A paraffin; citral; limonene; methyl anthranilate.
Linaloe (Lignaloe)	Mexican wood of *Bursera* species. *S. & Co.* Guiana wood (*Bois de rose femelle*).	0.880 0.875–0.895 0.875	-13 to +8 -5 to -12 -16.0	Fragrant oil. Resembles the Mexican wood oil.	Chiefly linalol, with terpineol, methyl-heptenone, and small amount of geraniol. Linalol (almost wholly).
Lovage	Dried root of *Levisticum officinale*. *B & Co.*	1.00–1.045 0.963–1.023	0 to +7 -14 to +12	Sol. in 2 to 3 parts of 80% alcohol.	d-terpineol; a terpene.
Mace	Arillode of seed of *Myristica fragrans*.	0.890–0.932	+10 to +20	Agreeable odour. Ref. index 1.476 to 1.484.	Pinene; dipentene; myristicin.
Mandarin	(See *Orange Oil, Mandarin*.)				
Marjoram	Fresh herb of *Origanum Marjorana*.	0.902–0.904	+20		
Marsh Tea (Ledum)	Herb of *Ledum palustre*. Leaves. Flowering twigs.	0.932 0.963		Pale reddish-yellow colour and penetrating odour. Boils between 180°–250°.	Terpenes (including terpinene, 40%; terpineol, 60%; traces of acetates and a sesquiterpene). Chief constituent said to be Ledum-camphor.

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot.°	Other characters	Known constituents
Masterwort..........	Root of *Imperatoria ostruthium*.	0.875	....	....	Angelic aldehyde (?).
Massory Bark........	Bark of *Massoia aromatica*.	1.04–1.06	....	Agreeable spicy odour reminding of clove and nutmeg, and a sharp burning taste.	Eugenol (75%); safrol; pinene; limonene; dipentene.
Mate................	Dried leaves of *Ilex Paraguayensis*.	0.887.5	+3.73 at 20°	Solid, melts at 26.5°. Sol. in absolute alcohol.	
Matico..............	Leaves (and flowers) of *Piper angustifolium*. Leaves....... / Flowers........	0.93–1.07 / 1.132	—1 to +6	Yellowish-brown colour and peculiar odour.	Dill-apiol; small amount of parsley-apiol; a phenol, possibly methyl-eugenol; a substance solidifying at −18°.
Meadowsweet........	Herb of *Spiræa ulmaria*.	....	....	....	Salicyl-aldehyde; a terpene.
Melaleuca..........	Leaves of { *Melaleuca acuminata*. / *M. leucadendron* / *M. uncinata*.	0.892 / 0.955 / 0.925	—15.3 / —3.7 / +1.7	....	Cineol; terpineol.
Melissa.............	Herb of *Melissa officinalis*.	0.895–0.925	—0.5 to —6.5	Ref. index 1.474 to 1.484.	Citral; citronellal; geraniol; linalol; citronellol.
Mew................	Dried root of *Meum athamanticum*.	1.001	....	Above 300° gives greenish-blue fractions.	
Michelia............	(See *Champaca Oil*.)				
Monarda (see Horse-mint Oil).	Herb of *Monarda punctata* (Horse-mint). / *M. fistulosa* (wild bergamot). / *M. citriodora*......	0.930–0.940 / 0.916–0.941 / 0.944 (at 20°)	Slightly + / Slightly — /	Thymol separates on standing.	Thymol 60%; cymene; traces d-limonene; linalol (?); carvacrol (?). / Carvacrol 55%; thymoquinone; thymo-hydroquinone; cymene; limonene. / Carvacrol; thymo-hydroquinone; citral 1%; cymene (?).

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TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot., °	Other characters	Known constituents
Mountain mint	Herb of *Pycnanthemum incanum.*	0.910–0.940	+3 to +5	....	Carvacrol; pulegone.
Mugwort	(See *Artemisia oil.*)				
Muskroot	Rhizome of *Ferula sumbul.*	0.950–0.964	....	Sol. in equal vol. of 90% alcohol.	
Mustard	*Sinapis nyra* (seeds).	1.014–1.032	0 to 1	Ref. index 1.525 to 1.535.	Allyl thiocyanate, carbon disulphide, cyaniry.
Myrcia	(See *Bay Oil.*)				
Myrtle	Leaves of *Myrtus communis.*	0.890–0.920	+10 to +30		Pinene; cineol; dipentene; linalol (?).
Neroli	(See *Orange-flower Oil.*)				
Nigella	Seeds of *Nigella sativa.* Seeds of *Nigella damascena.*	0.8:5 / 0.906	+1.5 / +1	Boils between 170° and 260°. Blue fluorescence.......	Damascenine.
Nikkei	Leaves and young twigs of *Cinnamomum loureirii.* Root Bark.	0.9005 / 0.982	−8.75	Yellow oil of pleasant odour, recalling citral and cinnamon	Aldehydes, 2?% chiefly citral; linalol (40%); cineol. Cinnamic aldehyde.
Nutmeg	Fruit of *Myristica fragrans.* *Brit. Pharm.* S. & Co.	0.870–0.910 / 0.865–0.920	+14 to +30	Darkens and thickens on exposure to air. Spicy taste. Ref. index 1.4760.	Chiefly pinene and myristicin.
Olibanum	Gum-resin of *Boswellia Carterii* and other species.	0.875–0.885	−11.5	Balsamic odour........	Chiefly lævo-pinene; some phellandrene; dipentene; cadinene; and oxygenated bodies.

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot., °	Other characters	Known constituents
Onion oil......	Fresh herb and bulb of *Allium cepa*.	1.035–1.045	– 5	Dark brown oil......	Allyl propyl disulphide. Allyl sulphide and terpenes are absent.
Orange flower (neroli oil).	Fresh flowers of *Citrus bigaradia* (Bitter Orange). S. & Co.	....	....	Fragrant odour and somewhat bitter taste.	Limonene (26%); linalol (30%); linalyl acetate (40%); geraniol (30%); nerol; a paraffin.
	Fresh flowers of *Citrus aurantium* (Sweet Orange).	0.870–0.885 0.870–08.90	to +10 +10 to +29	Ref. index 1.4755......	
Orange peel (by expression).	Fresh peel of *Citrus bigaradia* (Bitter Orange).	0.853–0.854	+91 to +98		Chiefly limonene. The oil from the sweet orange also contains citral with minute portions of oxygenated substances (citronelal and another aldehyde).
	Citrus aurantium (Sweet Orange). Expressed from unripe fruit.	0.848–0.852 0.853	+96 to +99 +76.8	Ref. index 1.472 to 1.478.	
Orange, mandarin......	Expressed from fresh peel of *Citrus madurensis*.	0.850–0.860	About +70	....	Limonene; citral; probably citronelal; methyl ester methyl anthranilate. Limettin (?).
Orange, tangerine......		0.859	+69	....	
Origanum......	Herb of *Origanum hirtum*.	0.940–0.980	Inactive or slightly –	Golden-yellow colour when freshly rectified, reddish or reddish-brown on keeping. Penetrating, aromatic, thyme-like odour.	Carvacrol (60 to 80%). Should not contain less than 50%.
	Herb of *Origanum smyrnæum*.	0.915–0.966	0 to +15	....	Cymol; linalol; carvacrol (30–60%). Ref. index 1.510.
Orris root......	Rhizomes of several species of *Iris* (*I. germanica* and *I. pallida*, etc.).	....	Slightly +	Melts at about 40° to 50°. Exquisite and persistent odour.	Myristic acid (about 90%); oleic acid; methyl oleate and myristate; oleic aldehyde; irone, 10 to 15%.
Orris otto......		0.9489	– 20.5	Soluble in 70% alcohol, 1:8. Congeals at –5°.	

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot., °	Other characters	Known constituents
Palmarosa	(See Geranium Oils.)				
Paracoto	Bark of a species of Monimiaceæ or Lauraceæ.	0.925–0.950	−1 to −4	Colourless oil of pleasant odour.	Cadinene; methyl-eugenol.
Parsley	Fruit of Petroselinum sativum. S. & Co.	1.05–1.10	−7.3	Colourless or pale greenish yellow. Ref. index 1.4890. Deposits crystals, probably apiol.	Pinene; apiol.
	Root of P. sativum.	1.00 to 1.05	−2 to +1.5		
Pastinac	Fruit of Pastinaca sativa.	0.870–0.890	−0.2 to −0.5	A yellow oil.	Ethyl alcohol; octyl butyrate; octyl propionate.
Patchouli	Leaves of Pogostemon patchouli. S. & Co.	0.975–0.995	−50 to −65	Yellowish-green or brown, somewhat thick oil, with a penetrating and persistent odour. Ref. index 1.5115.	Cadinene (?); cedrene; patchouli-camphor; a liquid sesquiterpene-alcohol; benzaldehyde; eugenol; cinnamic aldehyde; a ketone.
	Leaves of a species of Pogostemon (from Java).	0.961	−32.2	Occasionally deposits a stearoptene.	A substance having an odour resembling anise aldehyde.
Pennyroyal	(See Oil of Hedeoma.)				
Pepper	Fruit of Piper nigrum. S. & Co.	0.870–0.905	−5 to +2	Strong pungent odour and taste.	Phellandrene; dipentene.
	B. & Co.	0.930	−8.5		
	Fruit of Piper longum (Long pepper). S. & Co.	0.861	......	Thickish oil of a light green colour, odour reminding of ginger. Boils at 250°–300°.	
Pepper, Japanese	Fruit of Xanthoxylum piperitum.	0.973	......	......	Citral.

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot., °	Other characters	Known constituents
Peppermint oils......	*Mentha piperita*......	0.900–0.920	−18 to −33	Ref. index 1.465.	Menthol, menthyl acetate, etc.
Persea...............	Dried leaves of *Persea gratissima*.	0.960	+1.9	Greenish oil; refractive index at 18°, 1.5164.	Methyl-chavicol; pinene; paraffin.
Petit-grain..........	Leaves, twigs and unripe fruits of *Citrus bigaradia*. S. & Co. / B. & Co.	0.887–0.900 / 0.8907; 0.8908	−1.3 to +3.7 / −1.11; −3.8	Odour resembling neroli oil.	Limonene; linalol; nerol; linalyl acetate; a sesquiterpene..
Petit-grain citronnier.	Leaves and twigs of *Citrus medica*. S. & Co. / B. & Co.	0.869–0.874 / 0.878	+22 to +34 / +9.4	Contains oil from unripe fruit. /	Esters (as linalol), 4%; citral. / Esters (as linalol), 10%; citral, 11%.
Peucedanum..........	Root of *Peucedanum grande*.	0.900	+30 to +35	B. p. 185–228°, leaving large residue.	
Pichurim bean........	Seeds of *Nectandra pichury*.	....	....	Fraction distilling between 255° and 256° is of a deep blue colour.	Pinene; esters of lauric and valeric acids (?); safrol (?).
Pimento (allspice oil).	Nearly ripe fruit of *Pimenta officinalis*.	1.045–0.055	−1 to +1	Becomes darker and thicker by age and exposure to the air. Clove-like odour and pungent spicy taste.	Eugenol; a sesquiterpene. Closely resembles clove oil in composition and properties.
Pimpinella...........	Dried root of *Pimpinella saxifraga*.	0.960	....	Unpleasant odour resembling parsley. Boils at 240°.	
Pine-needles.........	(See *Pinus pumilio*)..	0.859–0.865	−3 to −10		
Pittosporum ("mock-orange").	Fruit of *Pimpinella undulatum*.	0.861	+74	....	Limonene, 75%; a sesquiterpene; traces of esters.

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot.,°	Other characters	Known constituents
Popular	Young buds of *Populus nigra*.	0.900-0.905	+2 to +6	Odour of chamomile. Boils at 260°.	Humulene and another sesquiterpene; a paraffin.
Pyrethrum (fever-few)	Flowering or dried herb of *Pyrethrum parthenium*.	0.900-0.960	……	Sap. value, 131.	Borneol and bornyl esters; camphor (?).
Ragweed	Flowering herb of *Ambrosia artemisi-folia*.	0.870	−26	Deep green colour.	
Rhodium	(See *Rosewood Oil*.)				
Rose	Fresh flowers of *Rosa damascena*.	0.853-0.858	−1 to −4	Fragrant odour, and mild, sweetish taste. Congealing-pt. about 16° to 21°. Ref. index 1.4580.	Geraniol; citronellol; a paraffin.
	Brit. Pharm.	0.856-0.860 (at 30°)			
	U. S. Pharm.	0.855-0.865 (at 25°)	……	Congeals at 18-22°.	Sap. value, 10-17.
	S. & Co.:— Bulgarian Oil	0.855-0.870 (at 20°)	0 to −4		
	German Oil	0.845-0.855 (at 30°)	+1 to −1		
Rosemary	Flowering tops of *Rosmarinus officinalis*. *Brit. Pharm.*	0.896-0.920	−9 to +18	……………	Pinene; camphene; cineol; camphor; borneol and bornyl acetate.
		0.900-0.915	To +10	……………	
Rosewood (rhodium)	Wood of *Convolvulus scoparius* and *C. floridus*.	0.900-0.910	Laevorotatory	Thick yellow oil of rose-like odour, crystallising in needles at about 12°. Commercial oil invariably mixture of rose and geranium oils, etc.	Apparently chiefly a sesquiterpene.

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot.°	Other characters	Known constituents
Rue	Herb of *Rua grave olens.* S. & Co.	0.833–0.840	+0.2 to +2.1	Greenish-yellow colour and characteristic odour. Solidifies at 8 to 10°. Boils at about 215–235°.	About 90% of methyl-nonyl-ketone; lauric aldehyde; small amounts of methyl-heptyl-ketone; methyl ester of methyl anthranilic acid.
Algerian		0.842	+5	Blue oil in high fractions (0.5%). Ketone solidifies at −16°. Both rue oils sol. in 2–3 vols. of alcohol (70%).	Methyl-heptyl-ketone; small amount of methyl-nonyl-ketone; an acetic ester; methyl-heptyl and methyl-nonyl carbinols; pinene; *l*-limonene; cineol, etc.
Saffron	Stigmas of *Crocus sativus.*				Pinene; cineol; a paraffin; an oxygenated body; palmitic and stearic acids.
Sage	Leaves of *Salvia officinalis.*	0.915–0.930	+12 to +25	Penetrating characteristic odour.	Thujone; borneol; pinene; cineol.
Sage (clary)	Leaves of *Salvia sclarea.* S. & Co.	0.907–0.928	−24	Odour of linalyl acetate.	Linalyl acetate (?).
Sandalwood	Wood of *Santalum album.*			Yellowish thick oil, peculiar odour and pungent spicy taste.	Santal alcohols (94 to 98%); santalol, 3%; *a* & *b*-santalenes; santalic acid; teresantalic acid; esters of santal alcohols.
Sandalwood. (East Indian)	*Brit. Pharm.* S. & Co.	0.975–0.980 0.970–0.980	−1.6 to −20 −17 to −19	Saponification figure of the pure oil does not exceed 15. Ref. index 1.505 to 1.510.	
(West Indian) (African)	Unknown. *B. & Co. S. & Co.* Unknown (from Madagascar). *S. & Co.*	0.971–0.982 0.963–0.967 0.969	−10.8 to −17.7 +24 to +29	Ruby-red colour.	
(W. Australian)	*S. cygnorum.*	0.953	+5.3	Sharp resinous empyreumatic odour.	Contains less santal alcohols than East Indian oils.

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot., °	Other characters	Known constituents
wood.—Con- Pyrethrum, Australian.)	S. Preissianum......	1.022	....	Cherry-red colour. Solidifies at about 6°.	A crystalline alcohol boiling at 101°-103°.
Sassafras.........	Leaves of Sassafras officinalis.	0.872	−6.5	....	Linalol; pinene; phellandrene; cadinene; a paraffin melting at 57°.
	Root-bark of S. officinalis.	1.065-1.095	+1 to +4	Reddish-yellow oil with a warm taste.	Safrol, 80%; camphor; pinene; phellandrene; eugenol; cadinene (?).
Satureja.........	Herb of Satureja Thymbra, S. & Co. Fresh herb of S. hortensis. S. & Co.	0.906 0.898-0.924	.... +0.1	Strong and penetrating thymol-like odour.	Cymol; thymol, 19%; pinene; dipentene; bornyl acetate. Carvacrol (30%); cymene (?); pinene (?); traces of another phenol.
	Herb of S. montana (Mountain Savory).	0.939	+2.5	Odour resembling common savory oil.	Carvacrol; and, according to Haller, another phenol and a terpene.
Savin.........	Twigs of Juniperus sabina. U. S. Pharm.	0.910-0.940 0.903-0.923 (at 25°.)	+40 to +60 (at 25°.)	Becomes darker and thicker by age and exposure to air. Terebinthinate odour and pungent camphoraceous taste. Boils at 208°.	Pinene; cadinene; sabinol, partly as acetate; cumin aldehyde (?).
Savory.........	(See Satureja Oils.)				
Serpentaria.........	Rhizome and roots of Aristolochia Serpentaria. ("Virginian Snakeroot.")	0.975-0.988	....	Amber colour, and an odour resembling valerian and camphor.	Pinene; an ester of borneol; and a bluish-green fraction.
Shaddock.........	(See Grape-fruit Oil.)				

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot., °	Other characters	Known constituents
Snake-root.........	(See *Asarum Canadense, A. Europaeum,* and *Serpentaria* Oils.)				•
Spearmint.........	Fresh herb of *Mentha viridis.* S & Co.	0.920–0.980	–30 to –50	Becomes darker and thicker by age and exposure to air. Strong characteristic odour and warm taste.	Carvone; pinene; limonene; linalol.
Spike............	(See *Lavender Spike* Oil.)				
Spicewood.........	Bark and twigs of *Laurus (Lindera) benzoin.*	0.923	......	Distils between 170°–300°.	Terpenes; methyl salicylate (10%).
Spoonwort.........	Fresh flowering plant of *Cochlearia officinalis.*	0.954	+55.5	Distils between 150°–162°, leaving 5% of residue.	Secondary butyl thiocarbimide.
Star anise	(See *Anise* Oil, *Star.*)				'
Sweet birch	Bark of *Betula lenta.*	1.175–1.187	Inactive.	Boils at 218–221°.	Methyl salicylate, 99.8%; an ester, and a paraffin, etc.
Tansy	Herb of *Tanacetum vulgare.* English Oil. S. & Co. (Fresh Herb. / Dried Herb.)	0.915–0.930 / 0.954	–27.5 / +30 to +45	Becomes brown on exposure to light and air. Poisonous.	Thujone ("tanacetone"); camphor; borneol.
Tansy balsam	Herb of *Tanacetum balsamita.* S. & Co.	0.943–0.949	–43.7 to –53.9	Balsamic odour, resembling common tansy. Distils between 283°.	Contains a paraffin.
Tarragon.........	(See *Estragon* Oil.)				

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot.,°	Other characters	Known constituents
Tetranthera	Fruit of *Tetranthera citrata.*	0.920			
Thuja	Leaves of *Thuja occidentalis* (so-called White Cedar). Commercial Oils. S. & Co.	0.915–0.925 0.922	−8 to −14 −6.1		Thujone; b-fenchone; pinene; inactive carvone.
	Root of *T. orientalis.*	0.979		Intense brown colour.	
Thyme	Leaves and flowering tops of *Thymus vulgaris.*	0.900–0.930	Slightly −	Yellowish-red oil, pungent, afterward cooling, taste. Ref. index 1.480 to 1.490.	Thymol, 20–30%; carvacrol; cymene; linalol; bornyl acetate; pinene ("thymene").
Thyme, wild	Dried herb of *Thymus Serpyllum,* S. & Co.	0.905–0.930	−1 to −11	Agreeable melissa-like aroma, with a slight odour of thyme.	Thymol; carvacrol; cymene.
	Herb of *T. camphoratus.*	0.904		Strong thyme-like odour reminding somewhat of origanum.	Carvacrol (?).
	Herb of *T. capitatus.*	0.901			Pinene; cymene; dipentene; bornyl acetate; thymol; carvacrol (?).
Tuberose	Flowers.			Odourous fraction distils at 80°–180° at 15 mm. pressure.	
Turmeric	Root of *Curcuma longa.*	0.940	Dextrorotatory.		Phellandrene.
Valerian	Root of *Valeriana officinalis.*	0.930–0.955	−8 to −15	Yellowish or brownish colour, characteristic. penetrating odour. Boils between 250–300°.	Pinene; camphene; limonene (?); borneol; bornyl formate, acetate and iso-valerate; terpineol (?); a sesquiterpene; an alcohol.
	Root of *Valeriana Celtica.*	0.967			
Japanese (Kesso oil)	Root of *V. officinalis,* var. *angustifolia.*	0.990–0.996	−8 to −15	Green.	Similar to European root oil but containing also kessyl acetate, and a blue fraction.
Mexican.	Root of *Valeriana Mexicana.*	0.949	Inactive.		Valeric acid (about 89%).

TABLE OF ESSENTIAL OILS.—CONTINUED.

Oil	Chief sources	Sp. gr. at 15°	Opt. rot.,°	Other characters	Known constituents
Verbena..........	Verbena officinalis...	0.890–0.900	−16 to +3		
Veti-vert..........	Grass, Vetivera zizanoides. S. & Co.	1.010–1.027	+25 to +40	Most viscid of all essential oils.	
	Réunion oil........	0.9995	+29 to +36		
Wartara..........	Seeds of Xanthoxylum species.	0.8714	+6.5	Coriander odour........	Linalol; dipentene; methyl cinnamate.
Wax-myrtle........	Leaves of Myrica cerifera.	0.886	−5.1		
Wintergreen........	Leaves of Gaultheria procumbens.	1.175–1.187	−0.45 to −1	Boils at 218–221°........	Methyl salicylate, 99%; an aldehyde.
Wormseed.......... American.	Flower-buds of Artemisia maritima var. Stechmanniana. (See Chenopodium Oil.)	0.930–0.935	Slightly −	Poisonous...........	Cineol; dipentene.
Wormwood..........	Green herb of Artemisia absinthium.	0.925–0.955		Dark green colour when distilled from green herb. Unpleasant odour. Markedly poisonous.	Thujone (free and as acetate); thujyl alcohol; phellandrene; palmitic acid; acetic and iso-valeric acids (as thujyl esters); a blue fraction.
Ylang-Ylang (cananga oil).	Flowers of Cananga odorata.			Delicious odour........	Pinene; linalol; geraniol; iso-eugenol; linalyl and geranyl acetates and benzoates; cadinene; a crystalline alcohol; and para-cresol methyl-ether.
	East Indian.......	0.930–0.950	−40 to −45		
	Java.............	0.910–0.940	−20 to −55		
Zedoary..........	Root of Curcuma Zedoaria.	0.99–1.01		Viscid dark coloured oil. Distils at 240°–300°.	Cineol; a crystalline body melting at 142.5°.

SOLUBILITY TABLE OF THE MOST USED ODORIFEROUS SUBSTANCES.

From Schimmel & Co's. Report.

S l. = less than 0.1 part per 100; ∞ = sol. in any proportion.

100 parts by weight of solvent dissolve at 10°	96% alcohol	70% alcohol	Glycerol	Olive oil	Paraffin oil
Anethole	20	3	s. l.[1]	10	6
Anisic aldehyde (Aubépine)	∞[2]	130	0.1	∞	1.5(opal.)
Benzaldehyde	∞	70	0.1	∞	7
Benzoic acid ethyl ester	∞	45	s. l.	∞	∞
Benzoic acid methyl ester	∞	65	0.1	∞	∞
Benzyl acetate	∞	50	0.1	∞	13
Benzyl alcohol	∞	∞	∞	∞	1
Benzyl benzoate	∞	3	s. l.	∞	18
Bornyl acetate	∞	30	s. l.	∞	∞
Cassia oil, artificial, Sch. & Co. (see Cinnamic aldehyde).					
Cinnamic aldehyde	∞	30	0.1	∞	1.5(opal.)
Cinnamic alcohol	∞	∞	1	11	0.7
Cinnamic acid benzyl ester	∞	1.5(cloudy)	s. l.	∞	4(opal.)
Cinnamic acid ethyl ester	∞	13	s. l.	∞	∞
Cinnamic acid methyl ester	∞	50	s. l.	∞	∞
Cinnamein (see Peru balsam oil).					
Citral	∞	40	s. l.	∞	∞
Citronellal	∞	25	s. l.	∞	∞(opal.)
Citronellol	∞	55	0.1	∞	∞
Coumarin	8	4	0.1	1.5	0.3
Eucalyptol	∞	55	0.1	∞	∞
Eugenol	∞	110	0.1	∞	3(opal.)
Geraniol	∞	65	0.1	∞	∞
Geranyl acetate	∞	6(cloudy)	s. l.	∞	∞
Geranyl methyl ether	∞	6(opal.)	s. l.	∞	∞
Heliotropin (Piperonal)	8	5	s. l.	6	0.8(opal.)
Hyacinth, Sch. & Co	∞ (opal.)	3(opal.)	s. l.	∞	2(opal.)
Isoeugenol	∞	115	0.1	∞	0.7(opal.)
Isosafrol	∞	2	s. l.	∞	∞
Jasmine, Sch. & Co.	∞	150	0.1	∞	2
Lilac, Sch. & Co.	∞	65	0.1	∞	∞
Lily of the Valley, Sch. & Co.	∞	100	0.1	∞	4
Linalool	∞	50	0.1	∞	∞
Linalyl acetate (Bergamiol)	∞	24	0.1	∞	∞
Menthol	300	23	0.1	10	10
Methylanthranilic acid methyl ester.	∞	7	s. l.	∞	∞
Musk, artificial, Sch. & Co..	0.5	s. l.	s. l.	2.5	0.7
Musk, artificial, Sch. & Co., extra soluble.	1.1	0.2	s. l.	2.5	0.7
Musk-seed (Ambrette) oil, Sch. & Co.	∞	2	s. l.	∞	∞
Muguet (see lily of the valley).					
Narcissus, Sch. & Co.	∞	95	0.1	∞	∞
Neoviolone 100%	∞	40	s. l.	∞	∞
Neroli, Sch. & Co	∞	35	s. l.	∞	∞
Nerolin I	5	0.8	s. l.	13	6
Nerolin II	2	0.4	s. l.	3	2
Niobe oil (see Benzoic acid methyl ester).					
Novoviol	∞	25	s. l.	∞	∞
Orris oil, liquid, Sch. & Co.	∞	6	s. l.	∞	∞
Orris oil, solid	10	s. l.	s. l.	2	0.8
Paracresol methyl ether	∞	10	0.1	∞	∞
Peru balsam oil	∞	1.5(opal.)	s. l.	∞ (opal.)	0.7(opal.)
Pheny ethyl alcohol	∞	∞	1.5	∞	1.5
Pink blossom oil, Sch. & Co.	∞	80	0.1	∞	1.5(opal.)
Reseda-Geraniol, Sch. & Co.	∞	50	0.1	∞	∞(opal.)

SOLUBILITY TABLE OF THE MOST USED ODORIFEROUS SUBSTANCES.—CONTINUED.

100 parts by weight of solvent dissolve at 10°	96% alcohol	70% alcohol	Glycerol	Olive oil	Paraffin oil
Rose oil, artificial, Sch. & Co.	20[1]	20[1]	s. l.	50	50
Rose oil, artificial, liquid, Sch. & Co.	∞	30[2]	s. l.	∞	∞
Rose oil, natural, free from stearoptene.	∞	30	s. l.	∞	∞
Safrole..................	∞	3	s. l.	∞	∞
Salicylic acid amyl ester...	∞	1	s. l.	∞	∞
Salicylic acid ethyl ester...	∞	7	s. l.	∞	∞
Salicylic acid methyl ester.	∞	11	0.1	∞	∞
Santalol.................	∞	25	0.1	∞	∞
Terpineol, liquid..........	∞	60	0.1	∞	∞
Thymene.................	∞	1	s. l.	∞	∞
Thymol..................	200	30	0.1	50	5
Trefol (see salicylic acid amyl ester).					
Vanillin.................	38	30	1	0.9	s. l.
Wallflower, Sch. & Co.....	∞	∞	0.1	∞	0.4(opal.)
Wintergreen oil, artificial (see salicylic acid methyl ester).					
Ylang-Ylang, Sch. & Co....	∞	40	s. l.	∞	∞

[1] Soluble with strong separation of paraffin; completely soluble only when greatly diluted.
[2] Soluble with slight separation of paraffin; completely soluble only when greatly diluted.

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